ADVANCED SEPARATIONS BY SPECIALIZED SORBENTS

CHROMATOGRAPHIC SCIENCE SERIES

A Series of Textbooks and Reference Books

Editor:
Nelu Grinberg

Founding Editor:
Jack Cazes

1. Dynamics of Chromatography: Principles and Theory, J. Calvin Giddings
2. Gas Chromatographic Analysis of Drugs and Pesticides, Benjamin J. Gudzinowicz
3. Principles of Adsorption Chromatography: The Separation of Nonionic Organic Compounds, Lloyd R. Snyder
4. Multicomponent Chromatography: Theory of Interference, Friedrich Helfferich and Gerhard Klein
5. Quantitative Analysis by Gas Chromatography, Josef Novák
6. High-Speed Liquid Chromatography, Peter M. Rajcsanyi and Elisabeth Rajcsanyi
7. Fundamentals of Integrated GC-MS (in three parts), Benjamin J. Gudzinowicz, Michael J. Gudzinowicz, and Horace F. Martin
8. Liquid Chromatography of Polymers and Related Materials, Jack Cazes
9. GLC and HPLC Determination of Therapeutic Agents (in three parts), Part 1 edited by Kiyoshi Tsuji and Walter Morozowich, Parts 2 and 3 edited by Kiyoshi Tsuji
10. Biological/Biomedical Applications of Liquid Chromatography, edited by Gerald L. Hawk
11. Chromatography in Petroleum Analysis, edited by Klaus H. Altgelt and T. H. Gouw
12. Biological/Biomedical Applications of Liquid Chromatography II, edited by Gerald L. Hawk
13. Liquid Chromatography of Polymers and Related Materials II, edited by Jack Cazes and Xavier Delamare
14. Introduction to Analytical Gas Chromatography: History, Principles, and Practice, John A. Perry
15. Applications of Glass Capillary Gas Chromatography, edited by Walter G. Jennings
16. Steroid Analysis by HPLC: Recent Applications, edited by Marie P. Kautsky
17. Thin-Layer Chromatography: Techniques and Applications, Bernard Fried and Joseph Sherma
18. Biological/Biomedical Applications of Liquid Chromatography III, edited by Gerald L. Hawk
19. Liquid Chromatography of Polymers and Related Materials III, edited by Jack Cazes

20. Biological/Biomedical Applications of Liquid Chromatography, edited by Gerald L. Hawk
21. Chromatographic Separation and Extraction with Foamed Plastics and Rubbers, G. J. Moody and J. D. R. Thomas
22. Analytical Pyrolysis: A Comprehensive Guide, William J. Irwin
23. Liquid Chromatography Detectors, edited by Thomas M. Vickrey
24. High-Performance Liquid Chromatography in Forensic Chemistry, edited by Ira S. Lurie and John D. Wittwer, Jr.
25. Steric Exclusion Liquid Chromatography of Polymers, edited by Josef Janca
26. HPLC Analysis of Biological Compounds: A Laboratory Guide, William S. Hancock and James T. Sparrow
27. Affinity Chromatography: Template Chromatography of Nucleic Acids and Proteins, Herbert Schott
28. HPLC in Nucleic Acid Research: Methods and Applications, edited by Phyllis R. Brown
29. Pyrolysis and GC in Polymer Analysis, edited by S. A. Liebman and E. J. Levy
30. Modern Chromatographic Analysis of the Vitamins, edited by André P. De Leenheer, Willy E. Lambert, and Marcel G. M. De Ruyter
31. Ion-Pair Chromatography, edited by Milton T. W. Hearn
32. Therapeutic Drug Monitoring and Toxicology by Liquid Chromatography, edited by Steven H. Y. Wong
33. Affinity Chromatography: Practical and Theoretical Aspects, Peter Mohr and Klaus Pommerening
34. Reaction Detection in Liquid Chromatography, edited by Ira S. Krull
35. Thin-Layer Chromatography: Techniques and Applications, Second Edition, Revised and Expanded, Bernard Fried and Joseph Sherma
36. Quantitative Thin-Layer Chromatography and Its Industrial Applications, edited by Laszlo R. Treiber
37. Ion Chromatography, edited by James G. Tarter
38. Chromatographic Theory and Basic Principles, edited by Jan Åke Jönsson
39. Field-Flow Fractionation: Analysis of Macromolecules and Particles, Josef Janca
40. Chromatographic Chiral Separations, edited by Morris Zief and Laura J. Crane
41. Quantitative Analysis by Gas Chromatography, Second Edition, Revised and Expanded, Josef Novák
42. Flow Perturbation Gas Chromatography, N. A. Katsanos
43. Ion-Exchange Chromatography of Proteins, Shuichi Yamamoto, Kazuhiro Naka-nishi, and Ryuichi Matsuno
44. Countercurrent Chromatography: Theory and Practice, edited by N. Bhushan Man-dava and Yoichiro Ito
45. Microbore Column Chromatography: A Unified Approach to Chromatography, edited by Frank J. Yang
46. Preparative-Scale Chromatography, edited by Eli Grushka
47. Packings and Stationary Phases in Chromatographic Techniques, edited by Klaus K. Unger

48. Detection-Oriented Derivatization Techniques in Liquid Chromatography, edited by Henk Lingeman and Willy J. M. Underberg
49. Chromatographic Analysis of Pharmaceuticals, edited by John A. Adamovics
50. Multidimensional Chromatography: Techniques and Applications, edited by Hernan Cortes
51. HPLC of Biological Macromolecules: Methods and Applications, edited by Karen M. Gooding and Fred E. Regnier
52. Modern Thin-Layer Chromatography, edited by Nelu Grinberg
53. Chromatographic Analysis of Alkaloids, Milan Popl, Jan Fähnrich, and Vlastimil Tatar
54. HPLC in Clinical Chemistry, I. N. Papadoyannis
55. Handbook of Thin-Layer Chromatography, edited by Joseph Sherma and Bernard Fried
56. Gas–Liquid–Solid Chromatography, V. G. Berezkin
57. Complexation Chromatography, edited by D. Cagniant
58. Liquid Chromatography–Mass Spectrometry, W. M. A. Niessen and Jan van der Greef
59. Trace Analysis with Microcolumn Liquid Chromatography, Milos Krejcl
60. Modern Chromatographic Analysis of Vitamins: Second Edition, edited by André P. De Leenheer, Willy E. Lambert, and Hans J. Nelis
61. Preparative and Production Scale Chromatography, edited by G. Ganetsos and P. E. Barker
62. Diode Array Detection in HPLC, edited by Ludwig Huber and Stephan A. George
63. Handbook of Affinity Chromatography, edited by Toni Kline
64. Capillary Electrophoresis Technology, edited by Norberto A. Guzman
65. Lipid Chromatographic Analysis, edited by Takayuki Shibamoto
66. Thin-Layer Chromatography: Techniques and Applications: Third Edition, Revised and Expanded, Bernard Fried and Joseph Sherma
67. Liquid Chromatography for the Analyst, Raymond P. W. Scott
68. Centrifugal Partition Chromatography, edited by Alain P. Foucault
69. Handbook of Size Exclusion Chromatography, edited by Chi-San Wu
70. Techniques and Practice of Chromatography, Raymond P. W. Scott
71. Handbook of Thin-Layer Chromatography: Second Edition, Revised and Expanded, edited by Joseph Sherma and Bernard Fried
72. Liquid Chromatography of Oligomers, Constantin V. Uglea
73. Chromatographic Detectors: Design, Function, and Operation, Raymond P. W. Scott
74. Chromatographic Analysis of Pharmaceuticals: Second Edition, Revised and Expanded, edited by John A. Adamovics
75. Supercritical Fluid Chromatography with Packed Columns: Techniques and Applications, edited by Klaus Anton and Claire Berger
76. Introduction to Analytical Gas Chromatography: Second Edition, Revised and Expanded, Raymond P. W. Scott
77. Chromatographic Analysis of Environmental and Food Toxicants, edited by Takayuki Shibamoto

78. Handbook of HPLC, edited by Elena Katz, Roy Eksteen, Peter Schoenmakers, and Neil Miller
79. Liquid Chromatography–Mass Spectrometry: Second Edition, Revised and Expanded, Wilfried Niessen
80. Capillary Electrophoresis of Proteins, Tim Wehr, Roberto Rodríguez-Díaz, and Mingde Zhu
81. Thin-Layer Chromatography: Fourth Edition, Revised and Expanded, Bernard Fried and Joseph Sherma
82. Countercurrent Chromatography, edited by Jean-Michel Menet and Didier Thiébaut
83. Micellar Liquid Chromatography, Alain Berthod and Celia García-Alvarez-Coque
84. Modern Chromatographic Analysis of Vitamins: Third Edition, Revised and Expanded, edited by André P. De Leenheer, Willy E. Lambert, and Jan F. Van Bocxlaer
85. Quantitative Chromatographic Analysis, Thomas E. Beesley, Benjamin Buglio, and Raymond P. W. Scott
86. Current Practice of Gas Chromatography–Mass Spectrometry, edited by W. M. A. Niessen
87. HPLC of Biological Macromolecules: Second Edition, Revised and Expanded, edited by Karen M. Gooding and Fred E. Regnier
88. Scale-Up and Optimization in Preparative Chromatography: Principles and Biopharmaceutical Applications, edited by Anurag S. Rathore and Ajoy Velayudhan
89. Handbook of Thin-Layer Chromatography: Third Edition, Revised and Expanded, edited by Joseph Sherma and Bernard Fried
90. Chiral Separations by Liquid Chromatography and Related Technologies, Hassan Y. Aboul-Enein and Imran Ali
91. Handbook of Size Exclusion Chromatography and Related Techniques: Second Edition, edited by Chi-San Wu
92. Handbook of Affinity Chromatography: Second Edition, edited by David S. Hage
93. Chromatographic Analysis of the Environment: Third Edition, edited by Leo M. L. Nollet
94. Microfluidic Lab-on-a-Chip for Chemical and Biological Analysis and Discovery, Paul C.H. Li
95. Preparative Layer Chromatography, edited by Teresa Kowalska and Joseph Sherma
96. Instrumental Methods in Metal Ion Speciation, Imran Ali and Hassan Y. Aboul-Enein
97. Liquid Chromatography–Mass Spectrometry: Third Edition, Wilfried M. A. Niessen
98. Thin Layer Chromatography in Chiral Separations and Analysis, edited by Teresa Kowalska and Joseph Sherma
99. Thin Layer Chromatography in Phytochemistry, edited by Monika Waksmundzka-Hajnos, Joseph Sherma, and Teresa Kowalska
100. Chiral Separations by Capillary Electrophoresis, edited by Ann Van Eeckhaut and Yvette Michotte
101. Handbook of HPLC: Second Edition, edited by Danilo Corradini and consulting editor Terry M. Phillips
102. High Performance Liquid Chromatography in Phytochemical Analysis, edited by Monika Waksmundzka-Hajnos and Joseph Sherma

103. Hydrophilic Interaction Liquid Chromatography (HILIC) and Advanced Applications, edited by Perry G. Wang and Weixuan He
104. Hyphenated and Alternative Methods of Detection in Chromatography, edited by R. Andrew Shalliker
105. LC-NMR: Expanding the Limits of Structure Elucidation, Nina C. Gonnella
106. Thin Layer Chromatography in Drug Analysis, edited by Łukasz Komsta, Monika Waksmundzka-Hajnos, and Joseph Sherma
107. Pharmaceutical Industry Practices on Genotoxic Impurities, edited by Heewon Lee
108. Advanced Separations by Specialized Sorbents, edited by Ecaterina Stela Dragan

ADVANCED SEPARATIONS BY SPECIALIZED SORBENTS

EDITED BY

ECATERINA STELA DRAGAN

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Version Date: 20140529

International Standard Book Number-13: 978-1-4822-2056-8 (eBook - PDF)

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

To my daughters, Irina and Ioana

Ecaterina Stela Dragan

Contents

Preface xiii
Editor xvii
Contributors xix

Chapter 1 Composite Hydrogel Materials 1
S. Kudaibergenov, Zh. Ibrayeva, M. Yashkarova, S. Kabdrakhmanova, and G. Tatykhanova

Chapter 2 Cryogels for Affinity Chromatography 39
Nilay Bereli, Deniz Türkmen, Handan Yavuz, Igor Yuri Galaev, and Adil Denizli

Chapter 3 Particulate/Cell Separations Using Macroporous Monolithic Matrices 69
Akshay Srivastava, Akhilesh Kumar Shakya, and Ashok Kumar

Chapter 4 Polysaccharide-Based Composite Hydrogels for Removal of Pollutants from Water 89
Junping Zhang and Aiqin Wang

Chapter 5 Iron Oxide Magnetic Composite Adsorbents for Heavy Metal Pollutant Removal 127
Doina Hritcu, Gianina Dodi, and Marcel Ionel Popa

Chapter 6 Biopolymer–Zeolite Composites as Biosorbents for Separation Processes 143
Maria Valentina Dinu and Ecaterina Stela Dragan

Chapter 7 Metal-Impregnated Ion Exchanger for Selective Removal and Recovery of Trace Phosphate 175
Sukalyan Sengupta and Arup K. SenGupta

Chapter 8 Molecularly Imprinted Polymers for Water Polishing 195
Joanna Wolska and Marek Bryjak

Chapter 9 Biopolymer-Based Sorbents for Metal Sorption 209

Eric Guibal, Thierry Vincent, and Ricardo Navarro

Chapter 10 Mixed-Mode Sorbents in Solid-Phase Extraction............................ 241

N. Fontanals, F. Borrull, and Rosa Maria Marcé

Chapter 11 Interpenetrating Polymer Network Composite Hydrogels and Their Applications in Separation Processes.............................. 281

Ecaterina Stela Dragan and Maria Valentina Dinu

Chapter 12 Toward Adaptive Self-Informed Membranes.................................. 311

Ioana Moleavin and Mihail Barboiu

Preface

This book provides a comprehensive overview of the advanced techniques employed to create specialized sorbents with a wide range of functions, which can be used to enhance the separation and/or purification of useful bioactive species like proteins and cells, heavy metal ions, dyes, etc. It illustrates some of the most efficient materials promoted in recent decades for the separation processes. The main purpose of this book is to update the scientific information in a field of research that is growing dynamically. Thus, the latest information in the field of separation processes by specialized sorbents like monolith cryogels, composite hydrogels, magnetic composite adsorbents, metal-impregnated ion exchangers, molecularly imprinted polymers, and solid phase extraction by mixed mode sorbents are presented and compared with the authors' results. Biobased polymer composites occupy a unique place in the dynamic world of new sorbents, and this book provides novel information on them. Readers will get updated information and an in-depth perspective on the design strategies, characterization, and application of novel sorbents. The material will also help researchers in the design of their projects on specialized sorbents for the separation and/or purification of ionic species. The chapters in this book have been contributed by a team of renowned scientists from around the world whose expertise will enlarge the visibility of some of the most effective sorbents and will provide readers an overall view on the efficiency of different separation techniques.

Chapter 1 presents composite hydrogel materials consisting of cross-linked homo- and copolymers of acrylamide and N-isopropylacrylamide with embedded clay minerals, metal nanoparticles, drugs, and proteins. Special attention has been paid to the metal complexes of linear polyampholytes, cross-linked polybetaines, and macroporous amphoteric gels. Molecularly and ion-imprinted polymers focusing on selective recovery of transition and rare earth metal ions are presented. The potential applications of composite hydrogel materials in the oil industry for cleaning the internal surface of main pipes, in catalysis as metal nanoparticles immobilized within hydrogel matrices, and in medicine and biotechnology as controlled release of drugs and proteins are also outlined.

The progress during recent decades in the field of affinity chromatography is presented in Chapter 2. Affinity chromatography is a very efficient method of protein purification. Recently, dye-ligand affinity chromatography and immobilized metal affinity separation have gained considerable attention in the purification of proteins, both in laboratory and large-scale applications, assuring higher specificity, purity, and recovery in a single chromatographic step, as well as cost efficiency and safety. Lately, cryogel materials have been considered as a novel generation of stationary phases in separation science. They have proven to be highly efficient in protein purification with many advantages, including large pores, short diffusion path, low pressure drop, and very short residence time for both adsorption and elution. These unique features make them attractive matrices for the chromatography of biomolecules, viruses, plasmids, and even whole cells.

Monoliths are uniform matrices without interparticular voids, having significant importance as a stationary phase in different modes of chromatography. The pores in monoliths form interconnected channels across the matrix, which provides high permeability for the convective flow of the mobile phase and a large surface area for the binding of analytes. The advantages of macroporous monoliths are discussed in Chapter 3. Macroporous monoliths can be composed of silica, polymer, metal oxides, and carbon-based materials. Unlike conventional columns, they can easily be chemically modified, and a single monolith can have different functionalities in the separation of many analytes. Macroporous monolithic matrices provide fast, efficient, and easy separation of large biomolecules such as proteins, nucleic acids, bacteria, mammalian cells, or particulate matter with low mass transfer resistance. This chapter describes the different types of monoliths and their working principles and applications in particulate/cell separations.

Over the last decade, a special area of focus has been the removal of heavy metals and dyes from the environment because of their nonbiodegradability and long-term toxicity, which make them very dangerous for human health. Biosorbents derived from polysaccharides like chitosan and alginate attracted a strong interest as a cost-effective alternative to the existing sorbents like activated carbon and synthetic ion exchangers. Due to high adsorption capacity, chitosan and alginate have been extensively used as biosorbents in wastewater remediation. The advantages and perspectives of using specialized polysaccharide-based composites in the removal of heavy metals and dyes are presented in Chapters 4 through 6 and in Chapters 9 and 11.

Traditional hydrogels from synthetic and/or natural polymers often have some limitations, such as low mechanical stability and poor biodegradability, which restrict their practical applications. Recently, polysaccharide-based composite hydrogels, a new group of materials at the interface of hydrogels, polymer/clay nanocomposites, and polysaccharides, have attracted much attention due to their unique properties. The latest developments on this type of hydrogels are reviewed in Chapter 4. The applications of novel composite hydrogels in the removal of pollutants, including heavy metals, dyes, and ammonium nitrogen in water, are reviewed. Due to the synergistic effect among polysaccharides, vinyl monomers, and clay minerals, many of the physicochemical properties, such as swelling ratio and rate, thermostability, and gel strength of composite hydrogels, are superior to their counterparts.

Chapter 5 is focused on the sorption of heavy metals by magnetic adsorbent particles, the so-called magnetic beads. The facile separation of magnetic sorbents from the aqueous phase is the main advantage, which differentiates them from the traditional adsorbents. Their efficient removal in a magnetic field followed by regeneration and reuse decreases the overall cost of water treatment. Due to their high applicative potential, composite materials containing iron oxide incorporated in functional polymeric supports are intensely studied. This chapter presents recent developments in the very important field of the magnetic separation of heavy metals by composite biosorbents.

Synthesis and characterization of some biosorbents based on chitosan, alginate, and cellulose, as biopolymer matrix, embedded with synthetic or natural zeolites and their applications for the removal of heavy metal ions and the separation of aqueous–organic mixtures are summarized in Chapter 6. Removal of dyes by chitosan–zeolite composites are also discussed. The sorption capacities and the pervaporation separation performances of biopolymer–zeolite composites are compared with those of raw zeolite, pristine biopolymer, or other biopolymer-based composites.

In recent decades, the wastewater treatment industry has identified the discharge of nutrients, including phosphates and nitrates, into waterways as a risk to natural environments due to the serious effects of eutrophication of the water bodies. An abundance of algal blooming in eutrophic water bodies can deplete dissolved oxygen in water, causing fish deaths. Accordingly, it is necessary and urgent to explore effective techniques for phosphate removal from wastewater. The development and performance of new phosphate-selective sorbents, referred to as hybrid anion exchangers (HAIX), are presented in Chapter 7. HAIX combines the durability and mechanical strength of polymeric anion exchange resins with the high sorption affinity of hydrated ferric oxide toward phosphate.

Different chemicals like medicines, pesticides, plastics components, or industry pollutants, all toxic to the endocrine system, are found in natural waters. These substances are poorly removed from solutions by conventional methods. The use of molecularly imprinted polymers offers the possibility of removing them as they have a high affinity and selectivity toward templates. Chapter 8 presents the methods of synthesis of such sorbents with a focus on their use in hybrid systems, which seems to be a promising alternative for the removal of endocrine-disrupting compounds.

Chapter 9 describes the sorption mechanisms and performances of biopolymers (chitosan and alginate) as a function of the type of functional groups, the pH, the composition of the solution, as well as the size and morphology of particles. Sorption may proceed through chelation/complexation, ion exchange/electrostatic attraction, or the formation of a ternary complex. The choice of the biopolymer depends on the target metal and the metal speciation. The versatility of these materials is of great interest for developing novel sorbents with improved diffusion properties, enhanced hydrodynamic behavior, and innovative application modes. In addition, these biopolymers can be used for encapsulating reactive compounds (ionic liquids, extractants, ion exchangers) in order to improve the reactivity, selectivity, or sorption efficiency of these materials, profiting from the possibility to condition these composite sorbents under different forms (beads, membranes, foams, etc.). Hybrid materials (e.g., metal-loaded biopolymers) can also be used to design new materials and new applications. Some examples are discussed that show how biopolymers can be given fresh life after metal binding.

Mixed-mode polymeric sorbents that enhance selectivity and capacity of extraction in a single material are described in Chapter 10. Different aspects of these materials are described, including their synthesis, morphological and chemical properties, as well as their application in solid-phase extractions (SPE). SPE protocols for each type of mixed-mode sorbents (strong/weak and cation/anion-exchange materials) are also discussed, since the protocols are crucial for the success of this kind of material. Applications of sorbents in different types of matrices are presented compared with commercial sorbents.

Single-network hydrogels have poor mechanical properties and slow responses at swelling. Various strategies, including the preparation of interpenetrating polymer network (IPN) hydrogels, have therefore been developed to remediate these weak points. The most significant classes of IPN composite hydrogels and their applications, mainly in the separation processes of dyes, heavy metal ions, and liquids, are presented in Chapter 11. Synthesis parameters such as cross-linker ratio, monomer concentration, and synthesis temperature are the key factors that determine the properties of the semi-IPN and IPN hydrogels, such as interior morphology, swelling kinetics, mechanical strength, etc. Sorption kinetics and reusability of IPN composite hydrogels are further enhanced by the synthesis of IPN hydrogels under the freezing temperature of the solvent (cryogels).

A rational approach for building molecular channels in hybrid organic–inorganic materials via the inorganic (sol–gel) transcription of dynamic self-assembled superstructures is presented in Chapter 12. The basic and specific molecular information encoded in the molecular precursors results in the generation of tubular superstructures in solution and in a solid state, which can be frozen in a polymeric hybrid matrix by the sol–gel process. These systems have been successfully employed to design solid dense membranes that function as ion channels and to illustrate how a self-organized hybrid material performs interesting and potentially useful transporting functions.

Furthermore, the book contains numerous illustrations and tables that will guide readers in advanced separation procedures. In conclusion, this book focuses on a variety of advanced techniques available for separation and/or purification of target ionic species and addresses the needs and challenges for future research in this growing field.

Editor

Dr. Ecaterina Stela Dragan is the head of the Functional Polymers Department, "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania.

Her research interests include the synthesis and characterization of ionic polymers, smart composite hydrogels, porous ionic nano- and microstructured materials, surface modification by polyelectrolytes, and separation by ion exchangers and biosorbents.

She is the author or coauthor of more than 140 publications in international journals, 12 book chapters, and 38 national patents. She has been involved in the publication of seven books, both as author and editor. She is also a reviewer for numerous international journals. Her individual impact factor is >77 and Hirsch index, h = 20.

Contributors

Mihail Barboiu
Adaptive Nanosystems Group
Institut Européen des Membranes
Montpellier, France

Nilay Bereli
Biochemistry Division
Department of Chemistry
Hacettepe University
Ankara, Turkey

F. Borrull
Department of Analytical Chemistry and Organic Chemistry
University of Rovira and Virgili
Tarragona, Spain

Marek Bryjak
Faculty of Chemistry
Division of Polymer and Carbon Materials
Wroclaw University of Technology
Wroclaw, Poland

Adil Denizli
Biochemistry Division
Department of Chemistry
Hacettepe University
Ankara, Turkey

Maria Valentina Dinu
Functional Polymers Department
"Petru Poni" Institute of Macromolecular Chemistry
Iasi, Romania

Gianina Dodi
Faculty of Chemical Engineering and Environmental Protection
"Gheorghe Asachi" Technical University of Iasi
Iasi, Romania

and

SCIENT
Research Center for Instrumental Analysis
Bucharest, Romania

Ecaterina Stela Dragan
Functional Polymers Department
"Petru Poni" Institute of Macromolecular Chemistry
Iasi, Romania

N. Fontanals
Department of Analytical Chemistry and Organic Chemistry
University of Rovira and Virgili
Tarragona, Spain

Igor Yuri Galaev
DSM Nutritional Products, DBC
Heerlen, The Netherlands

Eric Guibal
Center for Materials Research
Alès School of Mines
Alès, France

Doina Hritcu
Faculty of Chemical Engineering and Environmental Protection
"Gheorghe Asachi" Technical University of Iasi
Iasi, Romania

Zh. Ibrayeva
Laboratory of Engineering Profile
K.I. Satpaev Kazakh National Technical University
and
Institute of Polymer Materials and Technology
Almaty, Kazakhstan

S. Kabdrakhmanova
S. Amanzholov East-Kazakhstan State University
Ust-Kamenogorsk, Kazakhstan

S. Kudaibergenov
Laboratory of Engineering Profile
K.I. Satpaev Kazakh National Technical University
and
Institute of Polymer Materials and Technology
Almaty, Kazakhstan

Ashok Kumar
Department of Biological Sciences and Bioengineering
Indian Institute of Technology Kanpur
Kanpur, India

Rosa Maria Marcé
Department of Analytical Chemistry and Organic Chemistry
University of Rovira and Virgili
Tarragona, Spain

Ioana Moleavin
Centre of Advanced Research in Nanobioconjugates and Biopolymers
"Petru Poni" Institute of Macromolecular Chemistry
Iasi, Romania

Ricardo Navarro
Department of Chemistry
University of Guanajuato
Guanajuato, Mexico

Marcel Ionel Popa
Faculty of Chemical Engineering and Environmental Protection
"Gheorghe Asachi" Technical University of Iasi
Iasi, Romania

Arup K. SenGupta
Department of Civil and Environmental Engineering
Lehigh University
Bethlehem, Pennsylvania

Sukalyan Sengupta
Department of Civil and Environmental Engineering
University of Massachusetts, Dartmouth
North Dartmouth, Massachusetts

Akhilesh Kumar Shakya
Department of Biological Sciences and Bioengineering
Indian Institute of Technology Kanpur
Kanpur, India

Akshay Srivastava
Department of Biological Sciences and Bioengineering
Indian Institute of Technology Kanpur
Kanpur, India

G. Tatykhanova
Laboratory of Engineering Profile
K.I. Satpaev Kazakh National Technical University
and
Institute of Polymer Materials and Technology
Almaty, Kazakhstan

Deniz Türkmen
Biochemistry Division
Department of Chemistry
Hacettepe University
Ankara, Turkey

Thierry Vincent
Center for Materials Research
Alès School of Mines
Alès, France

Aiqin Wang
Center of Eco-material and Green Chemistry
Lanzhou Institute of Chemical Physics
Chinese Academy of Sciences
Lanzhou, Gansu, People's Republic of China

Joanna Wolska
Faculty of Chemistry
Division of Polymer and Carbon Materials
Wroclaw University of Technology
Wroclaw, Poland

M. Yashkarova
Semipalatinsk State Shakarim University
Semey, Kazakhstan

Handan Yavuz
Biochemistry Division
Department of Chemistry
Hacettepe University
Ankara, Turkey

Junping Zhang
Center of Eco-material and Green Chemistry
Lanzhou Institute of Chemical Physics
Chinese Academy of Sciences
Lanzhou, Gansu, People's Republic of China

1 Composite Hydrogel Materials

S. Kudaibergenov, Zh. Ibrayeva, M. Yashkarova, S. Kabdrakhmanova, and G. Tatykhanova

CONTENTS

1.1 Introduction 2
1.2 Immobilization of Nano- and Microsized Clay Minerals into the Hydrogel Matrix 2
  1.2.1 Preparation and Characterization of Organic–Inorganic Composite Materials Based on Poly(acrylamide) Hydrogels and Clay Minerals 2
  1.2.2 Potential Application of Composite Hydrogel Materials as "Pigs" for Cleaning of the Internal Surface of Main Pipes 5
1.3 Physicochemical and Catalytic Properties of Polymer-Protected and Hydrogel-Immobilized Gold, Silver, and Palladium Nanoparticles 6
  1.3.1 Stabilization of Gold and Silver Nanoparticles by Hydrophilic Polymers 6
  1.3.2 Immobilization of Polymer-Protected AuNPs and AgNPs within Hydrogel Matrix 7
  1.3.3 Catalytic Properties of Polymer-Protected PdNPs and AuNPs Immobilized within Hydrogels 8
1.4 Drug Delivery Systems Based on Cross-Linked Copolymers of Acrylamide and *N*-Isopropylacrylamide 10
  1.4.1 Hydrogel-Immobilized Local Anesthetic Drugs 11
  1.4.2 Controlled Release of Proteins from Stimuli-Responsive Hydrogels 14
1.5 Complexes of Linear Polyampholytes and Amphoteric Gels with Transition Metal Ions 16
  1.5.1 Complexation of Polybetainic or Polyzwitterionic Gels with Metal Ions 16
  1.5.2 Metal Complexes of Amphoteric Cryogels 18
1.6 Molecular Imprinted Hydrogels for Recovery of Metal Ions 20
1.7 Concluding Remarks 23
Abbreviations 23
References 24

1.1 INTRODUCTION

At present, composite hydrogel materials have attracted considerable interest in research and industrial spheres (Kudaibergenov et al. 2007, Pavlyuchenko and Ivanchev 2009). Composite polymer hydrogels consist of at least two components that exhibit a synergistic effect. According to the canons of thermodynamic compatibility, there are many possible structures of composite hydrogels starting from complete phase separation and ending to formation of structures consisting of polymer matrix and nano-, micro-, and macrosized inclusions. The nature of interaction between the components can have covalent, ionic, and donor–acceptor character and can be stabilized by hydrogen bonds, hydrophobic interactions, and entanglement of macromolecular chains producing interpenetrating and semi-interpenetrating polymer networks (IPNs) (Wu et al. 2006, Zhang et al. 2005). Due to their composite structure and unique properties such as improved mechanical, thermal, electrical, and optical characteristics, they have been found to have a wide application in medicine, membrane technology, optical engineering, and catalysis (Frimpong et al. 2006, Lao and Ramanujan 2004, Lu et al. 2003, Sershen et al. 2000, 2005). This chapter is devoted to composite hydrogel materials based on cross-linked homo- and copolymers of acrylamide (AAm) and *N*-isopropylacrylamide (NIPA) within which inorganic nano- and microparticles, polymer-protected metal nanoparticles, proteins, drugs, and low-molecular-weight ligands are immobilized. Physicochemical, physicomechanical, and catalytic properties and volume-phase transition (VPT) of composite hydrogel materials have been studied. Application aspects of composite hydrogel materials in oil industry and catalysis, for wastewater purification, and as drug delivery systems are also outlined.

1.2 IMMOBILIZATION OF NANO- AND MICROSIZED CLAY MINERALS INTO THE HYDROGEL MATRIX

1.2.1 Preparation and Characterization of Organic–Inorganic Composite Materials Based on Poly(acrylamide) Hydrogels and Clay Minerals

The properties of hydrogels can be modified by embedding inorganic materials, such as montmorillonite (MMT), bentonite, mica, silica, titanium and aluminum oxides, and sericite, within the gel matrix (Avvaru et al. 1998, Cheng et al. 2007, Kabiri and Zohuriaan-Mehr 2003, Kurokawa and Sasaki 1982, Lee and Yang 2004, Lin et al. 2001, Ray and Okamoto 2003, Starodoubtsev et al. 2000). The pioneering works to strengthen the mechanical properties of gel specimen by adding inorganic components were done by Haraguchi and colleagues (Haraguchi et al. 2003, 2013, Haraguchi and Li 2006, Haraguchi and Takehisa 2002). Gel sample made from MMT and NIPA is elastically stretched to about 10 times its original length (Haraguchi et al. 2002). Osada and colleagues (Gong et al. 2003, Nakayama et al. 2004, Tanaka et al. 2005) designed a series of double-network hydrogels with extremely high mechanical strength. This kind of nanocomposite hydrogel exhibited high transparency, high deswelling rate, and extraordinary mechanical properties with elongation at break in excess of 10^3%. In an organic/inorganic network structure, the clay sheets will act as effective multifunctional cross-linkers through ionic or polar interactions. The layered structure of clay minerals and their ability to swell in water allow monomers and polymer chains to diffuse into clay layers and act as additional cross-linker. The overall stability of composite materials directly depends on whether exfoliation or intercalation process takes place and on the choice of monomer or initiator that can be adsorbed to the clay surface (Abdurrahmanoglu et al. 2008, Essawy 2008, Jia et al. 2008, Xiang et al. 2006). Preparation of lightweight porous materials by templating hydrogels with a range of hydrophilic and hydrophobic scaffolding materials was explored (Rutkevičius et al. 2012). Submillimeter hydrogel slurries of polyacrylamide (PAAm) and gellan gum were templated with aqueous slurries of cement, gypsum, and clay–cement mixtures or alternatively dispersed in curable polydimethylsiloxane. After the solidification of the scaffolding material, the evaporation of a structured hydrogel produced porous composite material whose pores mimic the hydrogel mesostructure. This versatile hydrogel templating method can be applied to yield lightweight porous materials with a great potential for use in the building industry in heat and sound insulation panels, lightweight building blocks, porous rubber substitutes, and foam shock absorbers and as an alternative to aerated concretes. The poly(acrylamide-*co*-acrylate)/rice husk ash hydrogel composites and a series of poly(acrylic acid-*co*-acrylamide)/kaolin composites are applied as soil conditioner and superabsorbent and serve as release carrier of urea fertilizer in agricultural industry (Cândido et al. 2013, Lianga and Liu 2007, Lianga et al. 2007).

The effect of silica nanoparticles on the linear viscoelastic response of model polyacrylamide hydrogel (PAAH) systems was examined (Kalfus et al. 2012). The removal of methylene blue (MB) cationic dye from its aqueous solution was performed with the help of chitosan-g-poly(acrylic acid) (CTS-g-PAAc)/MMT nanocomposites as adsorbent (Wang et al. 2008). The influence of pH value, MMT content (wt.%), weight ratio (w.r.) of acrylic acid (AAc) to CTS, and adsorption temperature on the adsorption capacity of the nanocomposite was investigated. The results showed that the w.r. of AAc to CTS of the nanocomposites has great influence on adsorption capacities and introducing a small amount of MMT could improve the adsorption ability of the CTS-g-PAAc. The adsorption behaviors of the nanocomposite showed that the maximum adsorption capacity is 1859 mg/g for CTS-g-PAAc/MMT with 30 wt.% and w.r. of 7.2:1. The desorption studies revealed that the nanocomposite provided the potential for regeneration and reuse after MB dye adsorption. The synthesis of poly(acrylic acid)–bentonite–FeCo (PAAc-B-FeCo) hydrogel nanocomposite via ultrasound-assisted *in situ* emulsion polymerization was carried out (Shirsath et al. 2011). Addition of exfoliated bentonite clay platelets and FeCo increased the strength and stability of the hydrogel and assisted the adsorption of an organic pollutant. The response of the nanocomposite hydrogel was evaluated using a cationic dye, crystal violet under a different temperature, pH, and cavitation environment. The optimum temperature was found to be 35°C, and basic pH at 11 was responsible for the higher adsorption of dye due to dissociation of COO^- ions at higher pH.

Amphoteric semi-IPN nanocomposite hydrogels were prepared by graft polymerization of AAc onto starch in cationic polyacrylamide (CPAM)/bentonite nanocomposite aqueous dispersion (Xu et al. 2008). CPAM was used as both an intercalating agent to enlarge interlayer space and a linear polymer chain to fabricate the semi-IPN structure. X-ray diffraction (XRD) and TEM confirmed a successful intercalation of CPAM into bentonite. The results showed that the hydrogel was of a high swelling and compressive strength even under water content of more than 99%.

Highly swollen AAm/2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) hydrogels and AAm/AMPS/bentonite composite hydrogels were prepared by free radical solution polymerization in aqueous solutions of AAm with AMPS and a clay such as bentonite and a multifunctional cross-linker such as ethylene glycol dimethacrylate (Kundakci et al. 2008). Highly swollen AAm/AMPS and AAm/AMPS/bentonite hydrogels were used in experiments on the sorption of water-soluble monovalent cationic dye such as Lauth's violet (LV) (thionine). Swelling of AAm/AMPS hydrogels was increased up to 2,282%–12,603% in water and 921%–3,575% in LV solutions, while AAm hydrogels swelled 927% in water, and swelling of AAm/AMPS/bentonite hydrogels was increased up to 3,225%–15,421% in water and 1,360%–4,189% in LV solutions, while AAm/bentonite hydrogels swelled 828% in water.

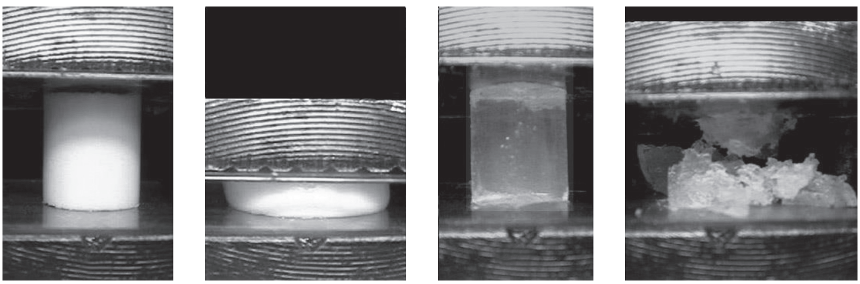
Both clay minerals embedded within neutral or charged hydrogel networks and linear charged macromolecules that stabilize clay minerals exhibit excellent absorbance capacity with respect to metal ions (Saber-Samandari and Gazi 2013) and dye molecules (Nakamura and Ogawa 2013, Shirsath et al. 2013, Yang and Ni 2012) and as a controlled-release drug carrier (Kevadiya et al. 2011). The nanocomposite hydrogels have much greater equilibrium swelling ratio, much faster response rate to pH, excellent thermal responsibility, and significantly improved tensile mechanical properties and high storage modulus (Xiang et al. 2006, Zhang et al. 2009).

The composite hydrogel materials based on clay minerals, TiO_2, SiO_2, and PAAH were obtained by one-step *in situ* polymerization (Svetlichnyy et al. 2009a). As a result, the flexible, elastic, and mechanically stable composite materials were designed. Swelling–deswelling behavior, VPT, and physicochemical, physicomechanical, and thermal properties of composite hydrogels have been studied (Ibrayeva 2010, Zhumaly et al. 2013). The mechanism of formation of the composite structures can be represented as diffusion of AAm monomers into the layered clay structure. After monomer intercalation into the space of minerals and polymerization with simultaneous cross-linking, composite hydrogel materials are formed where nano- and microsized clay particles play the role of additional physical cross-linking centers. It leads to a significant increase in mechanical properties of composite materials. The swelling degree of samples increases in the following order: PAAH/bentonite > PAAH/TiO_2 > PAAH/SiO_2 > PAAH/kaolin ≈ PAAH/MMT. For the PAAH/bentonite, PAAH/kaolin, PAAH/TiO_2, and PAAH/SiO_2 composites, the values of n that are between 0.6 and 0.94 correspond to an anomalous swelling mechanism, for example, non-Fickian diffusion. The effect of water–organic solvent mixture, pH, temperature, and ionic strength on the behavior of the composite materials was studied. Composite materials shrank in water–acetone and water–ethanol mixtures, as well as at high ionic strength of the solution, while changing of pH and temperature has no substantial influence. For the PAAH/kaolin and PAAH/bentonite composite hydrogels, the swelling degree decreased with increasing both the content of methylenebisacrylamide (MBAA) and bentonite, respectively. In the former case, it was connected with increasing of the density of chemical cross-links and, in the latter case, physical cross-links. Scanning electron microscopy (SEM) images revealed that the morphology of composite materials is represented as flat surface, cracks, and micropores with an average diameter of 5–10 μm. The XRD patterns are characterized by amorphous halo from PAAH followed by smaller peaks from clay minerals that are embedded within hydrogel matrix. The Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy results revealed that composite materials have not been simply a mechanical mixture of two components; in contrast, they were stabilized by hydrogen bonds between NH_2 groups of PAAH and oxygen groups of TiO_2, SiO_2, and aluminosilicates. The positive values of the enthalpy of mixing ΔH_m indicated that the swelling of PAAH/kaolin and PAAH/TiO_2 in water had endothermic character. It was shown that the thermal decomposition of composite hydrogel materials was shifted to a higher-temperature region in comparison with PAAH. The increase of kaolin quantity in PAAH volume led to reinforcing of mechanical properties of composite materials.

1.2.2 Potential Application of Composite Hydrogel Materials as "Pigs" for Cleaning of the Internal Surface of Main Pipes

Pipelines are used to transport the powders and fluids from one point to another. Pigging is an operation to remove debris or unwanted deposit buildup in a pipeline (Al-Yaari 2011, Jaggard and Allen 1977, Uzu et al. 2000). Debris, sand, and asphaltene–resin–paraffin depositions (ARPDs) in a pipeline will result in a pressure buildup, and if no pigging exists, their buildup could continue to rise and will create greater back pressure on the line, causing higher maintenance on pumps, and the line could eventually become blocked. It is forecasted that the composite hydrogel materials may bear more external load than that of pure hydrogel. In contrast to ordinary hydrogels, the composite materials consisting of hydrogels and clay minerals exhibit an improved physicomechanical property (Ibrayeva 2010, Svetlichnyy et al. 2009b). The mechanical stability of the PAAH/kaolin sample in comparison with pure PAAH is shown in Figure 1.1.

The laboratory device for study of the model oil pipeline is as follows: A slightly swollen hydrogel plunger (not miscible with oil) is immersed into the pipeline to



(a) (b) (c) (d)

FIGURE 1.1 Mechanical stability of PAAH/kaolin composite (a, b) and pristine PAAH (c, d) gels.

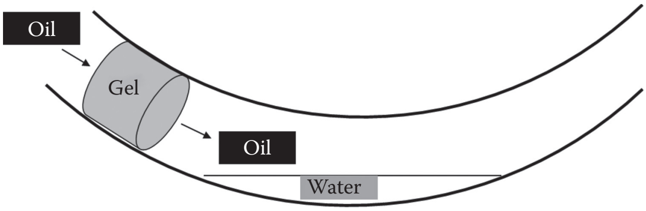


FIGURE 1.2 Schematic representation of cleaning of inner part of pipeline from APRD and water by hydrogel "pigs."

separate the oil flow. As the hydrogel "pig" moves along the pipe, it absorbs the water–saline solution and swells. The hydrogel swelling allows tight hydraulic sealing to the pipe wall. This, in turn, leads to efficient removal of gas accumulations, ARPD, mechanical impurities, and mineralized water from the pipeline inner cavity (Figure 1.2).

In cleaning a model pipeline from ARPD, the PAAH/kaolin composite hydrogel that showed the best elongation at break, tensile strength, and Young's modulus at 15 wt.% of kaolin was used (Zheksembayeva et al. 2012). The effectiveness of cleaning of deposited paraffins from Kumkol and Usen oil fields by composite hydrogel "pigs" ranges between 94% and 96% (Kudaibergenov et al. 2012a).

1.3 PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF POLYMER-PROTECTED AND HYDROGEL-IMMOBILIZED GOLD, SILVER, AND PALLADIUM NANOPARTICLES

1.3.1 Stabilization of Gold and Silver Nanoparticles by Hydrophilic Polymers

Gold (AuNPs) and silver (AgNPs) nanoparticles have attracted significant attention of researchers due to their unique optical, electrical, biomedical, and catalytic properties (Balasubramanian et al. 2010, Motoyuki and Hidehiro 2009, Shan and Tenhu 2007, Zhou et al. 2009). A lot of polymers possessing nonionic (Chung et al. 2012, Dai et al. 2007, Morrow et al. 2009, Ram et al. 2011), anionic (Dorris et al. 2008), cationic (Chen et al. 2012a), and amphoteric (Li et al. 2010, Mahltig et al. 2010, Note et al. 2007) nature are widely used as protecting agents of AuNPs and AgNPs in aqueous solution or organic solvents for preventing nanoparticle aggregation (Bekturov et al. 2010, Ibrayeva et al. 2013).

The size of poly(*N*-vinylpyrrolidone) (PVP)-protected AuNPs ranging from 10 to 110 nm was easily controlled by varying the concentration (0.01–10 g/dL) (Ram et al. 2011) or the average-number molecular weight of PVP (M_n = 10–350 kDa) (Yesmurzayeva et al. 2013). The shape, size, and optical properties of the AuNPs and AgNPs are tuned by changing the employed PVP/metal salt ratio (Hoppe et al. 2006). It is proposed that PVP acts as the reducing agent suffering a partial degradation during the nanoparticle synthesis. Two possible mechanisms are proposed to explain the reduction step: direct hydrogen abstraction induced by the metal ion and/or reducing action of macroradicals formed during degradation of the polymer. The initial formation of the macroradicals might be associated with the metal-accelerated decomposition of low amounts of peroxides present in the commercial polymer. Gold catalysts have recently attracted rapidly growing interests due to their potential applicabilities to many reactions of both industrial and environmental importance (Haruta 1997). Typical examples are the low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of carbon oxides and unsaturated hydrocarbons, and reduction of nitrogen oxides (Haruta and Daté 2001). A recent review (Shiju and Guliants 2009) describes the size-, shape-, structure-, and composition-dependent behavior of AuNPs employed in alkylation, dehydrogenation, hydrogenation, and selective oxidation reactions for the conversion of hydrocarbons (with main emphasis on fossil resources) to chemicals. The perspectives of substituting platinum group metals for automobile emission control with gold were outlined by authors (Zhang et al. 2011).

1.3.2 Immobilization of Polymer-Protected AuNPs and AgNPs within Hydrogel Matrix

Hydrogels are chemically stable and interlocked polymeric networks that retain vast amounts of water without dissolving; therefore, they are feasible for the preparation of metal nanoparticles *in situ* and readily applicable in the catalysis of various aquatic and nonaquatic reactions. The functional groups in the hydrogel network can act as both chelating and capping agents for metal nanoparticle preparation from metal ions and for their stabilization; thus, the metal particles are protected from the atmosphere hindering the oxidation/deactivation and aggregation, allowing an increase in their stability and longevity. Various synthesis methods have been reported to produce AuNPs–hydrogel composites (Dolya et al. 2013): (1) preparation of the nanoparticles and hydrogels, separate or in combination (Pardo-Yissar et al. 2001, Sheeney-Hai-Ichia et al. 2002); (2) mixing and polymerization of the preformed nanoparticles with monomer precursor(s) (Holtz and Asher 1997, Lee and Braun 2003, Sershen et al. 2000, 2001, Weissman et al. 1996); and (3) embedding of metal salts into a hydrogel matrix followed by a reduction process in the presence of reducing agents (Wang et al. 2004). The role of hydrophilic polymers in this system is to stabilize the metal nanoparticles and to prevent their aggregation, while the role of hydrogel matrix is restriction of diffusion of nanoparticles both inside of and outside from the gel matrix (Kudaibergenov 2008). A typical example of embedding of PVP-protected AuNPs, AgNPs, and palladium nanoparticles (PdNPs) within the hydrogel matrix is shown in Figure 1.3.

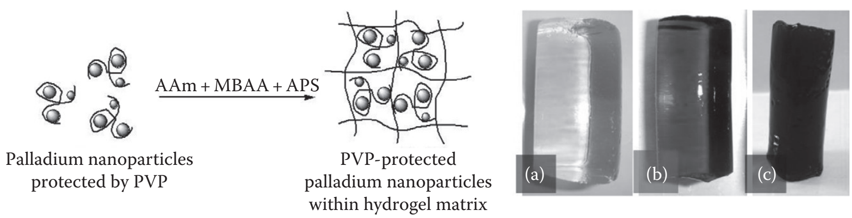


FIGURE 1.3 Immobilization protocol of polymer-protected nanoparticles within hydrogel matrix and PAAH samples with immobilized AgNPs (a), AuNPs (b), and PdNPs (c).

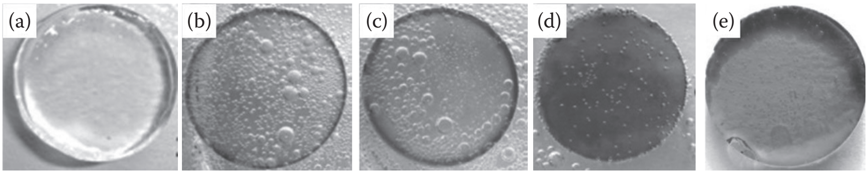


FIGURE 1.4 Swollen in water PAAH/PEI-$HAuCl_4$ (a) in the course of reduction by $NaBH_4$ (C = 0.1 mol/L) during 5 min (b), 15 min (c), 60 min (d), and 1 day (e).

The average size of AgNPs, AuNPs, and PdNPs in the volume of PAAH was equal to 20–30, 10–50, and 10–60 nm, respectively (Kudaibergenov et al. 2008). Metal ions with different oxidation states to be loaded into the hydrogel matrices can be reduced/precipitated to their metallic particle forms inside hydrogels of different dimensions using green chemicals or nontoxic chemical reducing agents such as $NaBH_4$, H_2, citrate, and ethylene glycol, depending upon the nature of the metal ions. Reduction of polyethyleneimine (PEI) protected and immobilized within PAAH AuNPs by $NaBH_4$ is shown in Figure 1.4 (Dolya 2009).

Reduction of PEI–Au^{3+} complexes to Au^0 within hydrogels is accompanied by the formation of a thin, colored layer on the gel surface that gradually moves into the gel volume. The driving force of this process is the constant diffusion of the reducing agent $NaBH_4$ deeply into the gel volume. Narrow-dispersed gold nanospheres and single crystals were prepared, respectively, by reducing $HAuCl_4$ within the hydrogel matrix (Kim and Lee 2007, Zhang et al. 2007). The authors (Kim and Lee 2007) described a unique strategy to prepare discrete composite nanoparticles consisting of a large gold core (60–150 nm) surrounded by a thermoresponsive hydrogel derived from the polymerization of NIPA or copolymerization with AAc. The growth of AuNPs in the presence of preformed spherical hydrogel particles allows a precise control of the size of composite nanoparticles between 200 and 550 nm. Most of the hydrogel-immobilized PdNPs exhibited good catalytic activity in both Heck and Suzuki reactions (Hagiwara et al. 2001, Kohler et al. 2001) and Suzuki–Miyaura cross-coupling reaction (Leadbeater and Marco 2002, Lu et al. 2004, Phan et al. 2004, Sivudu et al. 2008, Wu et al. 2011).

1.3.3 Catalytic Properties of Polymer-Protected PdNPs and AuNPs Immobilized within Hydrogels

The combination of natural catalytic abilities with the *in situ* metal nanocatalyst preparation capability makes hydrogels indispensable multifunctional materials for unique applications (Jiang et al. 2004, Kidambi et al. 2004, Metin et al. 2009, Sahiner 2004, Wunder et al. 2011). The recent review (Sahiner 2013) summarizes application aspects of metal nanoparticles within hydrogel templates in catalysis. Of special interest are the homo- and copolymers of NIPA that undergo a sharp volume transition around the body temperature (Peppas et al. 2006). Many researchers have examined the potential application of NIPA-based polymers for the immobilization of AuNPs (Echeverria and Mijangos 2010, Wang et al. 2004a,b).

Examples of catalytic system acting by "on-off" mechanism are NIPA-based hydrogels that reversibly swell or shrink in water–ethanol mixture (Wang et al. 2000) or reversibly turn "off" first and then "on" as the temperature is first raised and then lowered (Bergbreiter et al. 1998). The "smart" behavior of the PNIPA/PVP-Pd(0) system was demonstrated in the course of allyl alcohol hydrogenation (Dolya 2009, Dolya et al. 2008a,b, 2009). Swelling–deswelling of PNIPA at temperature interval 25°C–40°C causes the release or inflow of PVP-Pd(0) outside or inside of the hydrogel matrix. This in turn leads to periodic increase or decrease of the hydrogenation rate of allyl alcohol (Figure 1.5).

The catalytic activity of polymer-protected and PAAH-immobilized Pd(0) catalysts increased in the following order: PAAH/PVA-Pd(0) > PAAH/PVP-Pd(0) > PAAH/PEI-Pd(0) > PAAH/PAA-Pd(0). The catalytic activity of PAAH/PEI-Pd(0), PAAH/PVP-Pd(0), and PAAH/PVA-Pd(0) catalysts preserved up to hydrogenation of 12 sequential portions of allyl alcohol (Zharmagambetova et al. 2010). Turnover numbers (TONs) for PAAH/PEI-Pd(0) and PAAH/PVP-Pd(0) were equal to 4×10^3

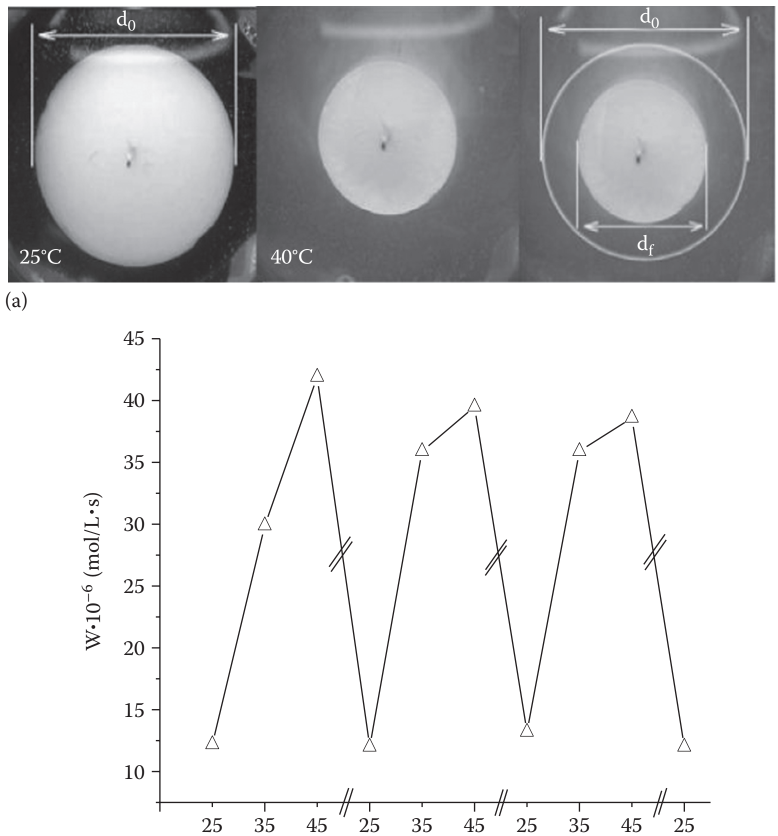
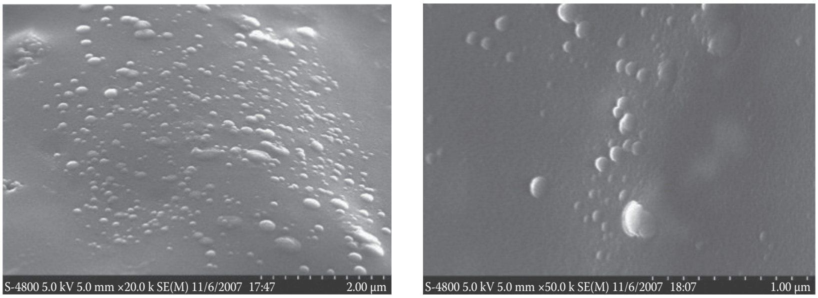


FIGURE 1.5 Reversible changing of size (a) and catalytic activity of PNIPA/PVP-Pd(0) (b) at 25 h 40°C.



(a) (b)

FIGURE 1.6 SEM pictures of PVP-protected PdNPs within the gel matrix of PAAH after hydrogenation of the 1st (a) and 12th (b) successive portions of allyl alcohol.

and 7×10^3, respectively, indicating a stable and long-lived behavior of catalysts. After hydrogenation of sequential portions of allyl alcohol, the amount of Pd(0) on the surface of gel matrix is considerably reduced (Figure 1.6). This is probably due to leaching out of Pd nanoparticles in the course of hydrogenation reaction. The average size of Pd nanoparticles was less than 100 nm, although the bigger aggregated particles were observed, while SEM micrographs of pristine PAAH/PVP-Pd(0) show spheres with an average diameter of about 60 nm that are related to PVP-stabilized spherical PdNPs or particle aggregates.

The catalytic activity of gel-immobilized AuNPs was evaluated with respect to hydrogen peroxide decomposition. The influence of (1) substrate concentration (C = 10–40 wt.%) at constant temperature (T = 328 K) and constant mass of catalyst (m_{cat} = 30 mg), (2) temperature (T = 308–323 K) at constant substrate concentration ($[H_2O_2]$ = 30 wt.%) and constant mass of catalyst (m_{cat} = 30 mg), and (3) mass of catalyst (m_{cat} = 15–50 mg) at constant temperature (T = 328 K) and constant substrate concentration ($[H_2O_2]$ = 30 wt.%) on the decomposition rate of H_2O_2 was studied. In each experiment, the volume of substrate was kept constant and equal to 1 mL.

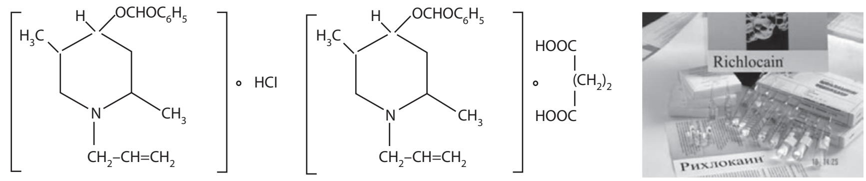
The catalytic activity of gel-immobilized AuNPs was much lower than that deposited on metal oxides. This is probably accounted for the less accessibility of catalytic centers in gel matrix to substrate molecules, for example, entrapment of polymer-protected AuNPs within hydrogel networks may restrict the diffusion of substrate inside of the gel.

1.4 DRUG DELIVERY SYSTEMS BASED ON CROSS-LINKED COPOLYMERS OF ACRYLAMIDE AND *N*-ISOPROPYLACRYLAMIDE

Immobilization of biologically active substances, such as drugs, proteins, DNA, enzymes, and living cells, within stimuli-responsive hydrogels is of great interest for medicine, pharmaceutics, biotechnology, and bio- and genetic engineering (Hoffman and Stayton 2004, Lee and Yuk 2007, Liu et al. 2007, Peppas et al. 2006, Rzaev et al. 2007, Stein 2009). One of the serious problems of modern medicine is transportation of biologically and physiologically active substances to target places of organisms in a strictly definite dose. Presently, about 25% of drugs of leading pharmaceutical companies prepared for selling, production, and application are provided by transportation system. Hydrogel materials, due to excellent swellability in water, softness, elasticity, and biological compatibility, are widely applied for the design of drug delivery systems that are able to transport drugs to a target part of an organism by realization of positive feedback with environment providing afterward more reliable and controlled treatment of diseases (Anish and Abdul 2012, Eros et al. 2003, Galaev and Mattiasson 1999, Kumar et al. 2007, Manpreet et al. 2013). Among the well-known hydrogel systems of synthetic origin, the homo- and copolymers of AAc and NIPA are able to change morphology, size, and shape under the action of external stimuli (Bajpai et al. 2008, Feng et al. 2010, Hoare and Kohane 2008, Jagur-Grodzinski 2010, Qiu and Park 2012). pH medium and body temperature changes are the most widely used triggering signals for both site-specific therapy and pulsatile drug release (Anil 2007, Bajpai et al. 2008, Coughlan et al. 2004, Liusheng et al. 2011, Yoshida et al. 2013). In this connection, the development of thermo- and pH-responsive hydrogel materials that might realize "on-off" mechanism of drug delivery, that is, opening and closing the "thermo- or pH valve" to deliver the dosed amount of drug to the diseased part of the body, presents great interest (Chen et al. 2012b). The most significant weakness of external stimuli-sensitive hydrogels is that their response time is too slow. Therefore, the fast-acting hydrogels are necessary, and the easiest way of achieving that goal is to make thinner and smaller hydrogels. A method for making thermally responsive hydrogel scaffolds with a remarkably rapid response to temperature changes was developed by Cho et al. (2008). The recent remarkable review of Klinger and Landfester (2012) presents some of the important fundamental examinations on the influence of (tunable) network characteristics on loading and release profiles and basic synthetic concepts to realize these concepts and highlights several examples of different approaches to stimuli-responsive microgels for loading and release applications.

1.4.1 Hydrogel-Immobilized Local Anesthetic Drugs

Immobilization of local anesthetic drugs, such as lidocaine, novocaine, and bupivacaine, into stimuli-responsive hydrogel matrix is very important to solve the problems of "medicine of catastrophe" when first aid is needed after an earthquake and fire. Hydrogel-immobilized local anesthetic drugs can serve as wound dressing materials due to their versatility and unique properties, such as high water content and soft and rubbery consistency, that make them similar to natural tissues. Literature survey shows that lidocaine was loaded within IPNs based on PNIPA, PVP, and AMPS (Akdemir and Kayaman-Apohan 2007) and NIPA–itaconic acid (IA) copolymeric hydrogels (Taşdelen et al. 2004) by sorption immobilization. Lidocaine uptake of the IPNs was found to increase from 24 to 166 (mg lidocaine/g dry gel) with increasing amount of AMPS contents in the IPN structure, while lidocaine adsorption capacity of the NIPA-IA hydrogels was found to increase from 3.6 to 862.1 (mg lidocaine/g dry gel) with increasing amount of IA in the gel structure. In both cases, the electrostatic interactions between anionic groups of hydrogels and cationic groups of lidocaine are responsible for retarding drug release profile. The release characteristics of lidocaine from an anionic hydrogel composed of carbopol and a cationic hydrogel composed of chitosan were examined for optimizing hydrogel formulation as a sponge filler to stop the bleeding and as a carrier for delivering lidocaine to relief pain after a tooth extraction (Liu et al. 2007). The elasticity of the gel matrix and the ionic complexing effect between the anionic acid groups of hydrogels and cationic groups of lidocaine are two main factors influencing regulation of the diffusion coefficient for controlling drug release. Spherical nanoparticulate drug carriers made of poly(D,L-lactic acid) (Gorner et al. 1999, Polakovič et al. 1999) and of poly(D,L-lactic-*co*-glycolic acid) 50:50 mol/mol (Holgado et al. 2008, Zhang et al. 2008) with controlled size were designed for encapsulation of lidocaine and bupivacaine. Particles with sizes in the range of 250–820 nm and low polydispersity were prepared with good reproducibility; the large particles with a high loading (~30%) showed under *in vitro* conditions a slow release over 24–30 h, the medium-sized carriers (loading of ~13%) released the drug over about 15 h, and the small particles with small loading (~7%) exhibited a rapid release over a couple of hours. Two simple models, diffusion and dissolution, were applied for the description of the experimental data of lidocaine release and for the identification of the release mechanisms for the nanoparticles of different drug loading. The modeling results showed that in the case of high drug loadings (about 30% w/w), where the whole drug or a large part of it was in the crystallized form, the crystal dissolution could be the step determining the release rate. On the other hand, the drug release was diffusion controlled at low loadings (<10% w/w) where the solid drug was randomly dispersed in the matrix. The estimated values of the diffusion coefficient of lidocaine in these particles were in the range of $(5–7) \times 10^{-20}$ m^2/s. The efficacy and toxicity of bupivacaine loaded in biodegradable polymer poly(sebacic-*co*-ricinoleic acid) for producing motor and sensory block when injected near the sciatic nerve were evaluated (Shikanov et al. 2007). *In vitro* and *in vivo* bupivacaine release after injection in mice showed that 70% of the drug has been released during 1 week. Single injection of 10% bupivacaine in the polymer caused motor and sensory block that lasted 30 h. It was concluded that the poly(sebacic-*co*-ricinoleic acid) is a safe carrier for prolonged activity of bupivacaine. Richlocaine and richlocaine hemisuccinate are new local anesthetic drugs, invented by Kazakhstan chemists, that have been registered and approved for use in CIS countries (Sharifkanov et al. 2011) (Figure 1.7). In medicine, richlocaine is applied only as an isotonic injection solution. The anesthetic and antibacterial effectiveness of richlocaine is much higher than that of bupivacaine, novocaine, and lidocaine.



(a) (b) (c)

FIGURE 1.7 Structural formulas of (a) richlocaine, (b) richlocaine hemisuccinate, and (c) richlocaine as an injection solution.

Development of a prolonged drug dosage form would be beneficial. Richlocaine was immobilized into linear and weakly cross-linked PVP (Makysh et al. 2003), poly(sodium acrylate) (PSA), and betaine-type polyampholyte gels (Makysh et al. 2002). The properties of polymer–drug complexes were studied with respect to external factors, such as pH, temperature, and thermodynamic quality of water–ethanol mixture. The kinetics of richlocaine release from the PVP gel matrix into water was studied. At pH = 7.0, ~20% of richlocaine was released within 96 h. This quantity remained constant up to 384 h, indicating poor desorption of richlocaine. Comparatively, complexes of richlocaine with PSA and betaine-type polyampholyte gels displayed better desorption; the degree of release of richlocaine reached ~95% within 144 h and ~80% within 260 h, respectively. The quantity of released richlocaine increased up to 50% at pH = 8.0, obviously indicating the destruction of the PVP gel–richlocaine complex at this pH. The activation energies of drug release from the PVP gel matrix, PSA gel, and betaine-type polyampholyte gel were equal to 6.86, 5.26, and 17.14 kJ/mol, respectively. The effect of richlocaine on the swelling/deswelling kinetics and pulsatile drug release from the thermoresponsive hydrogels such as weakly cross-linked copolymers of AAm-AAc, hydrogels of PNIPA, and 3D networks of NIPA-AAc and NIPA-AMPSA was examined (Tatykhanova 2009). The richlocaine release profile exhibits a similar trend with the swelling–deswelling behavior of hydrogels (Figure 1.8). The initial release of the drug is due to the presence of surface-encapsulated components that are squeezed out during the first temperature pulse. The release of richlocaine at T < volume phase transition temperature (VPTT) is governed by diffusion. At T > VPTT, the surface of the hydrogel shrunk immediately and formed an impermeable "skin" layer restricting the release of immobilized bioactive molecules. The second and third temperature pulses lead to the decrease of the release rate due to the decrease in the concentration of richlocaine in the hydrogel volume.

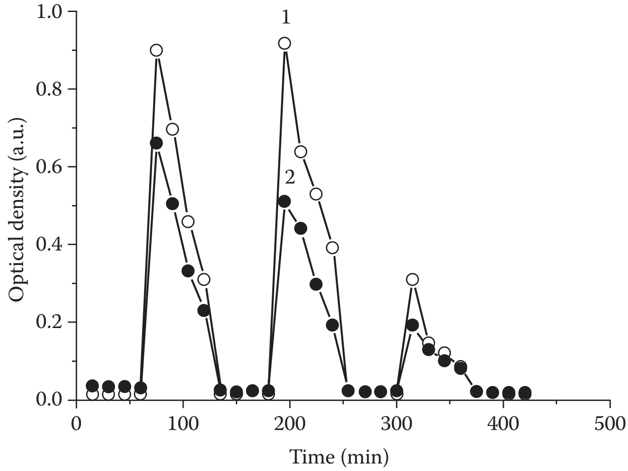


FIGURE 1.8 Time-dependent pulsatile release of richlocaine from PNIPAM hydrogel into phosphate buffer (1) and water (2) at 25°C and 40°C.

1.4.2 Controlled Release of Proteins from Stimuli-Responsive Hydrogels

The use of stimuli-sensitive hydrogels for the encapsulation and controlled release of proteins has received significant attention. The release of bovine serum albumin (BSA), a model drug, from a series of thermosensitive silk sericin (SS)/PNIPA and pH-responsive SS/poly(methacrylic acid) IPN hydrogels has been studied (Wen et al. 2013). The pulsatile releasing behavior of IPN hydrogels revealed that they can be made into microcapsules or thermo valves, which act as an on-off release control.

An efficient strategy to conjugate methacrylamide moieties to the lysine units of lysozyme for copolymerization and subsequent triggered release from hydrogels has been developed (Verheyen et al. 2011). Methacrylated dextran (dex-MA) was polymerized in the presence of native or modified lysozyme to yield hydrogels. The release of native and modified lysozyme from dex-MA hydrogels was studied in acetate buffer (pH 5, in the absence of any trigger), and only a minor fraction (~15%) of the modified lysozyme was released, whereas ~74% of the native lysozyme was released.

Horseradish peroxidase and alkaline phosphatase were immobilized into cellulose hydrogel prepared from an aqueous alkali–urea solvent (Isobe et al. 2011). Proteins were covalently introduced to cellulose gel by a Schiff base formation between the aldehyde and the amino groups of proteins and stabilized by a reduction of imines. The number of oxidized glucose per 100 glucose residues ranged between 3.3 and 18.6. The activity of the immobilized enzymes increased with aldehyde content, but the effect leveled off at a low degree of oxidation, at approximately 8.1 of oxidized glucose/100 glucose unit. The amount of immobilized peroxidase calculated from the activity was 8.0 ng/g for an aldehyde content of 0.18 mmol/g and 14.6 ng/g for both 0.46 and 1.04 mmol/g. Due to the high mechanical and chemical stability of cellulose, this technique and resulting materials are potentially useful in biochemical processing and sensing technologies.

Shi et al. (2008) studied the pH-sensitive release of lysozyme from the poly(*N*-vinyl formamide) nanogels ~100 nm in diameter. Approximately 95% of lysozyme encapsulated in nanogels released over 200 min at pH 5.8 compared to only ~15% released at pH 7.4.

β-Galactosidase was immobilized in a cross-linked PNIPA-AAc hydrogel that exhibits a VPT behavior (Park 1993). The stability of an immobilized enzyme was investigated at different temperatures that allow different degrees of collapse in the hydrogel matrix. It was hypothesized that the immobilized enzyme is more stable in the collapsed matrix due to the physical restraint imposed on the enzyme entrapped.

Temperature- and pH-sensitive hydrogels, based on NIPA and IA, were characterized for their sensitivity to the changes of external conditions and the ability to control the release of a hydrophilic model protein, lipase (Milasinovic et al. 2010). The hydrogels demonstrated protein loading efficiency as high as 95 wt.%. High dependence of lipase release kinetics on hydrogel structure and the environmental pH was found, showing low release rates in acidic media (pH 2.20) and higher at pH 6.80. The hydrogels were found suitable for releasing therapeutic proteins in a controlled manner at specific sites in the gastrointestinal tract.

Catalase was entrapped in PAAm, PSA, and poly(acrylamide-*co*-sodium acrylate) (PAAm-SA) gels (Jiang and Zhang 1993) and in thermally reversible poly(NIPA-*co*-hydroxyethylmethacrylate) (NIPA-HEMA) copolymer hydrogels (Arica et al. 1999) and on a cross-linked macromolecular carrier of a polysaccharide structure (gellan) (Popa et al. 2006). The percentage of entrapment was found to be about 85%. The enzyme immobilized in PAAm has very low activity, while the enzyme in PAAm-SA exhibits the highest activity. The kinetic behavior of the entrapped enzyme was investigated in a batch reactor. The apparent kinetic constant of the entrapped enzyme was determined by the application of the Michaelis–Menten model and indicated that the overall reaction rate was controlled by the substrate diffusion rate through the hydrogel matrix. Due to the thermoresponsive character of the NIPA-HEMA, the maximum activity was achieved at 25°C with the immobilized enzyme. The K_m value for immobilized catalase (28.6 mM) was higher than that of free enzyme (16.5 mM). Optimum pH was the same for both free and immobilized enzyme. Operational, thermal, and storage stabilities of the enzyme were found to increase with immobilization.

BSA and lysozyme were embedded into the hydrogel volume of AAm-AAc, PNIPA, and NIPA-AAc by *in situ* and sorption methods from aqueous and phosphate buffer solutions (pH = 7.4, μ = 0.15 M NaCl) (Kudaibergenov et al. 2011). Oscillating the "on-off" release mechanism of proteins from the volume of PNIPA and NIPA-AAc hydrogels was observed in the course of cyclic shrinking and swelling of hydrogels in water and phosphate buffer at 25°C and 40°C (Figure 1.9).

Sorption of catalase by AAm-AAc, NIPA-AAc, and PNIPA hydrogels proceeds via diffusion. Equilibrium swelling degree of dry samples in the course of catalase sorption and the activity of immobilized enzyme are changed in the following order: AAm-AAc > NIPA-AAc > PNIPA (Tatykhanova 2009). It is explained by the fact that binding of catalase by hydrogel matrix proceeds via electrostatic interaction with participation of carboxylic groups of the network and amine groups of enzyme.

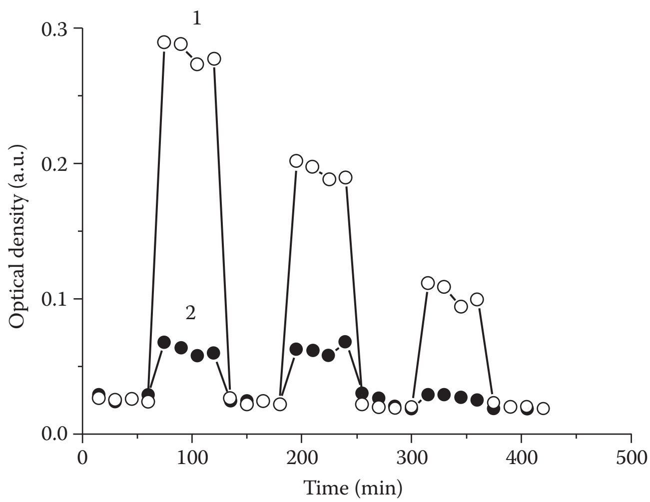


FIGURE 1.9 Time-dependent pulsatile release of BSA (1) and lysozyme (2) from PNIPAM hydrogel into phosphate buffer at 25°C and 40°C.

Maximal swelling and binding degree of catalase by hydrogels corresponds to neutral region. The relative activity of catalase encapsulated into AAm-AAc and NIPA-AAc networks after 74 days decreases two times, while the activity of catalase in solution decreases 46 times. The activity of immobilized and pristine catalase at temperature interval from 25°C to 70°C decreased 3 and 10 times, respectively. These results reveal that hydrogel-immobilized catalase preserves the catalytic activity for a long time and high temperature.

1.5 COMPLEXES OF LINEAR POLYAMPHOLYTES AND AMPHOTERIC GELS WITH TRANSITION METAL IONS

Renewed interest to polyampholyte–metal complexes is dictated by the fact that such complexes can model the protein–metal complexes and are relevant to catalysis (Bekturov and Kudaibergenov 1996, Casoloro et al. 2001, Khvan et al. 1985). For example, the kinetics and mechanism of complexation of AAc and vinylimidazole copolymers with Cu^{2+}, Co^{2+}, and Ni^{2+} ions are similar to the interaction of the carboxyl and imidazole groups of gelatin with the same metal ions (Annenkov et al. 2000, 2003). Polyampholyte–metal complexes are proved to exhibit catalase-like activity in decomposition of hydrogen peroxide (Bekturov et al. 1986, Lázaro Martínez et al. 2011, Sigitov et al. 1987) and to serve as hydrogenation or oxidation catalysts for organic substrates (Lázaro Martínez et al. 2008a,b, Xi et al. 2003). The ability of water-soluble or water-swelling polyampholytes to form stable chelate structure can be used for water treatment (Anderson et al. 1993) and recovery of metal ions from the wastewater (Ali et al. 2013, Chan and Wu 2001, Martınez et al. 2008, Rivas et al. 2006, Terlemezian et al. 1990, Xu et al. 2003) and polluted soils (Rychkov 2003). Amphoteric hydrogels, due to their high sorption and easy desorption of organic molecules and metal ions, coupled with durability and good mechanical stability, have potential applications in the removal of dyes (Dalaran et al. 2011) and recovery of metal ions from wastewater and in ion-exchange chromatography (Arasawa et al. 2004, Jiang and Irgum 1999). Amphoteric gel derived from ethylene glycol diglycidyl ether, methacrylic acid, and 2-methylimidazole has been complexed with Cu^{2+} and Co^{2+} ions (Lombardo Lupano et al. 2013, Martínez et al. 2011). The catalytic activity of this material was studied with respect to H_2O_2 decomposition. In the presence of polyampholyte–metal complexes, about 70% of methyl orange (model dye) was removed from distilled water in 2 h by oxidation with H_2O_2, and about 80% of epinephrine (model drug) was converted to adrenochrome in less than 6 min, following a pseudo-first-order kinetic model.

1.5.1 Complexation of Polybetainic or Polyzwitterionic Gels with Metal Ions

Among the various types of polyampholyte–metal complexes summarized in Ciferri and Kudaibergenov (2007), Kudaibergenov (2002), Kudaibergenov (2008), Kudaibergenov and Ciferri (2007), less attention has been paid to metal complexes of cross-linked polybetaines or polyzwitterions (Kudaibergenov et al. 2006). The polybetaines (or “polyzwitterions”) are dipolar species, in which the cationic and

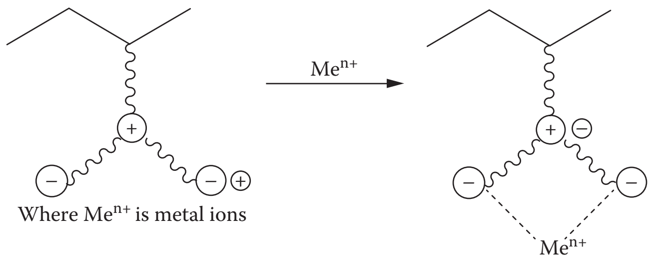


FIGURE 1.10 Simultaneous complexation of two units in CPZA is the driving force to capture Sr^{2+} ions.

anionic groups are separately bound to the same monomer unit and can be completely dissociated in a medium of sufficient dielectric permittivity. The most widespread chemical classes of polybetaines are carbo-, sulfo-, and phosphobetaines, that is, polymers with repeat units bearing simultaneously a quaternized ammonium group and a carboxylate, a sulfonate, or a phosphate group, respectively. As distinct from classical polybetaines, the research group of Ali (Ali and Haladu 2013, Ali and Hamouz 2012, Charles et al. 2012) developed novel polymers containing zwitterionic (±) and anionic (–) or cationic (+) groups such as poly(electrolyte–zwitterions) that have two negative and one positive charges (or two positive and one negative charges) in each monomer unit. The cross-linked polymer having zwitterionic/anionic group was synthesized via copolymerization of *N*,*N*-diallyl-*N*-sulfopropylammonioethanoic acid and sulfur dioxide in the presence of cross-linker 1,1,4,4-tetraallylpiperazinium dichloride followed by hydrolysis with NaOH to convert poly(zwitterions) into cross-linked polyzwitterion/anion (CPZA) (Ali and Haladu 2013). Simultaneous complexation of two units in CPZA is the driving force to capture Sr^{2+} ions (Figure 1.10).

The removal of 87% and 92% of Sr^{2+} ions at the initial concentrations of 200 ppb and 1 ppm was, respectively, observed. Excellent adsorption and desorption capacity of CPZA would enable its use in the treatment of radioactive nuclear waste containing Sr^{2+} ions.

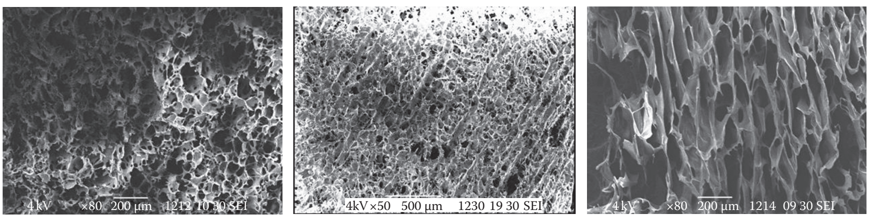
New amphoteric gels based on NIPA and amino acid (L-ornithine) were prepared by free radical polymerization in aqueous solutions (Marcin et al. 2010). The presence of NIPA and amino acid moieties imparts their multiresponsive character to temperature, pH, and metal ion complexation. The gels were found to be most sensitive to concentrations of copper ions in the range 10^{-6} to 10^{-5} M. As the amount of amino acid in the polymer network increases, the gels gradually lose their temperature sensitivity and become more sensitive to copper ion concentration. The VPTT decreases significantly after the addition of copper ions. Analysis of the UV-Vis spectra and the swelling behavior indicates that both 1:1 and 1:2 complexes are present in the swollen state of the gels, whereas the latter complex is more dominant in the shrunken state. It is concluded that the metal ion sorption ability, the temperature, and the pH sensitivity of amphoteric hydrogels make them interesting materials in terms of the temperature- and pH-triggered swinging of the binding strength of heavy metal absorbers.

Novel monomers containing amino acid residues were synthesized by condensation of the acetoacetic ester with glycine, β-alanine, and L-lysine in mild conditions (Kudaibergenov et al. 2007). Cross-linked polybetaines consisting of the amino acid moieties beside the carboxybetaine functionality were obtained via Michael addition reaction with participation of AAc followed by radical polymerization (Kudaibergenov et al. 2007). A series of polybetaine gels consisting of amino acid moieties (glycine, β-alanine, and L-lysine) were used to uptake metal ions from model solutions. Sorption of metal ions by hydrogels is accompanied by contraction and colorization of samples. At first, the thin colored layer on the gel surface is formed and it gradually moves into the gel volume. The driving force of this process is "ion-hopping transportation" of metal ions through intra- and intermolecular chelate formation, for example, constant migration of metal ions deeply into the gel volume by exchanging of free ligand vacancies.

1.5.2 Metal Complexes of Amphoteric Cryogels

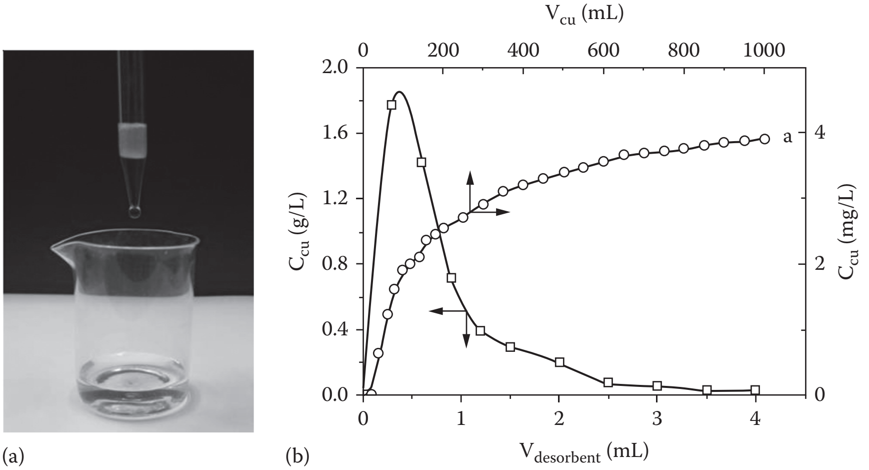
Cryogels are gel matrices that are formed in moderately frozen solutions of monomeric and polymeric precursors (Dinu et al. 2013, Mattiasson et al. 2010, Stein 2009). A system of large interconnected pores is a main characteristic feature of cryogels. The pore system in such spongelike gels ensures unhindered convectional transport of solutes within the cryogels, contrary to diffusion of solutes in traditional homophase gels. Semi-IPN cryogels based on cross-linked PAAm and anionic (Dragan and Apopei Loghin 2013) or cationic (Dragan and Dinu 2013) polyelectrolytes can serve as effective sorbents for the removal of dye molecules and metal ions. Amphoteric cryogels due to their response to temperature, pH, ionic strength, water–organic solvent composition, electric field, etc., belong to "smart" materials (Kudaibergenov et al. 2012b). A series of amphoteric cryogels with molar ratio of AAm, allylamine (AA), and methacrylic acid (MAA) (AAm:AA:MAA = 80:10:10, 60:20:20, 40:30:30, 20:40:40, and 0:50:50 mol.%/mol.%/mol.%) were synthesized (Kudaibergenov et al. 2012b, Tatykhanova et al. 2012). The structure and morphology of amphoteric cryogels and their complexation ability with respect to transition metal ions were evaluated. Cross and longitudinal sections of dry cryogels show spongelike porous structure with pore size ranging from 50 to 200 μm and the interconnected channels (Figure 1.11).

Complexation of amphoteric cryogels with transition metal ions is accompanied by colorization and slight shrinking of samples (Figure 1.12a). This is due to the formation of coordination and ionic bonds between metal ions and amine and/or



(a) (b) (c)

FIGURE 1.11 SEM images of cross- and longitudinal sections of cryogels with pore size (a) 50, (b) 100, and (c) 200 μm.

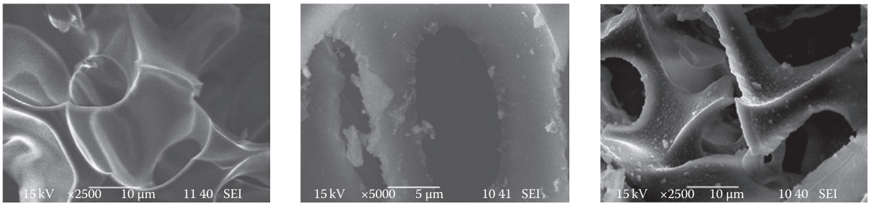


(a) (b)

FIGURE 1.12 Sorption (a) and desorption (b) of copper ions by amphoteric cryogel ACG-334.

carboxylic groups of cryogels when aqueous solutions of metal salts pass through the gel specimen. The dynamic sorption capacity of amphoteric cryogels with respect to copper, nickel, and cobalt ions was evaluated. The amount of adsorbed metal ions varied from 99.17% to 99.55%. Dynamic exchange capacity of cryogels was in the range of 350–400 mg/L. Desorption of metal ions from cryogel volume was provided by disodium salt of ethylenediaminetetraacetic acid. The extracted amount of metal ions was equal to 75%–80%. Figure 1.12b demonstrates the adsorption and desorption curves of copper ions by amphoteric cryogel.

Preferentially, the adsorption of Cu^{2+} ions (79%) in comparison with Ni^{2+} (38%) and Co^{2+} ions (32%) from their mixture was also observed from aqueous solution containing 10^{-5} mol/L of metal ions indicating the specific binding of copper ions. High adsorption capacity of amphoteric macroporous gels with respect to metal ions may be perspective for purification of the wastewaters and analytical purposes. The reduction of cryogel–metal complexes by $NaBH_4$ leads to the formation of nano- and micron-sized particles of metals and/or metal oxides immobilized on the inner and surface parts of amphoteric cryogels (Figure 1.13). The chemical composition of the Ni-containing sample by energy-dispersive x-ray attached to SEM revealed that up to 34 wt.% of Ni particles is formed.



(a) (b) (c)

FIGURE 1.13 SEM pictures of pristine (a) ACG-334/copper(II) complexes, (b) ACG-334/nickel(II), and (c) ACG-334/cobalt(II) complexes reduced by $NaBH_4$.

The following advantages of amphoteric macroporous cryogels with respect to metal ions are outlined: (1) Adsorption of metal ions can be provided in static and dynamic regimes; (2) adsorption and desorption processes are simple, for example, metal containing aqueous solution or desorbing agent is passed through the sample with definite rate; (3) high adsorption capacity of cryogels is due to the presence of complex-forming ligands (amine and carboxylic groups) and highly developed inner and outer surface; (4) the trace amount of metal ions may be concentrated up to three orders; (5) immobilized within macropores, metal ions can easily be reduced by reducing agents, and afterward cryogels might be used as flowing catalytic microreactors.

1.6 MOLECULAR IMPRINTED HYDROGELS FOR RECOVERY OF METAL IONS

Molecular recognition processes found in nature have always inspired scientists to mimic these systems in synthetic materials such as molecular imprinted polymers (MIPs) (Bergmann and Nicholas 2008, Byrne et al. 2002). MIPs and molecular imprinted hydrogels (MIHs) are commonly accepted in literature as synthetic approaches to design a precise macromolecular architecture for the recognition of target molecules from an ensemble of closely related molecules, while molecular imprinted technology (MIT) or molecular recognition technology (MRT) can be defined as engineering applications of such materials. Molecular imprinting involves forming a prepolymerization complex between the template molecule and functional monomers or functional oligomers (or polymers) (Wizeman and Kofinas 2001) with specific chemical structures designed to interact with the template by either covalent (Wulff 1995) or noncovalent chemistry (self-assembly) (Mosbach and Ramstrom 1996, Sellergren 1997), or both (Kirsch et al. 2000, Whitcombe et al. 1995). In the last decade, there has been an exponential increase in the number of papers describing molecular imprinting technique that creates memory for template molecules within a flexible macromolecular structure (Byrne and Salian 2008). Cameron et al. (2006) comprehensively surveyed over 1450 original papers, reviews, and monographs, starting from the pioneering work of Polyakov (1931) to show the fundamental and engineering aspects of molecular imprinting science and technology for the years up to and including 2003. According to the Web of Knowledge database searched up to 2012, ca. 13,000 papers have been published on molecular imprinting. Several remarkable reviews (Buengera et al. 2012, Byrne and Salian 2008, Hendrickson et al. 2006, Mayes and Whitcombe 2005, Romana et al. 2012, Tokonami et al. 2009, Vasapollo et al. 2011) were published with the aim to outline the molecularly imprinted process and present a summary of principal application fields of molecularly imprinted polymers, focusing on chemical sensing, separation science, biochemical analysis, drug delivery, catalysis, microfluidic devices, and analytical purposes.

The nature of the interaction between the functional monomers and the template with the formation of the complex has both covalent (covalent molecular imprinting) and noncovalent (noncovalent molecular imprinting) characters. Covalent molecular imprinting refers to imprinting of preorganized systems where the monomer–template complex is formed by the covalent interactions. Pioneering works of Nishide and Tsuchida (Nishide et al. 1976) and Kabanov (Kabanov et al. 1977, 1979) served as the fundamental basis for the imprinting of metal ions to MIPs. Such kind of polymeric sorbents made from natural and synthetic materials is widely used for the recovery of metal ions from the wastewater (Ahmadi et al. 2010, Bessbousse et al. 2012, Birlik et al. 2007, Chauhan et al. 2005, 2009, Ge et al. 2012, Godlewska-Zyłkiewicz et al. 2012, Kowalczyk et al. 2013, Li et al. 2010, Orozco-Guareño et al. 2010, Panic et al. 2013, Wawrzkiewicz 2013). Noncovalent imprinting belongs to imprinting of self-organizing systems in which the prepolymerization complex is formed by hydrogen, ionic bonding, hydrophobic and π–π interactions, as well as the van der Waals forces (Andersson and Mosbach 1990, Dunkin et al. 1993, Nicholls et al. 1995, Sellergren et al. 1985). The noncovalent imprinting approach seems to hold more potential for the future of molecular imprinting due to the vast number of compounds, including biological compounds, which are capable of noncovalent interactions with polymerizable monomers. These noncovalent interactions are easily reversed, usually by wash in aqueous solution of an acid, a base, or organic solvents, thus facilitating the removal of the template molecule from the network after polymerization.

The commonly accepted procedure for immobilization and leaching of imprinted metal ions is (a) *mixing* solutions of the functional monomer with a print molecule to afford the corresponding complex as the template, (b) *copolymerization* of the monomer–metal complex with the cross-linking agent in the presence of the initiator, (c) *washing* the crude copolymer to remove unreacted functional monomer, and (d) *leaching* the print molecule from the template to afford the MIP. Novel ion-imprinted polymers (IIPs) were used for selective solid-phase extraction of Cd(II) (Fan et al. 2012, Li et al. 2011, Singh and Mishra 2009), Pb(II) (Behbahani et al. 2013), Cu(II) (Chen and Wang 2009, Shamsipur et al. 2010), and Ni(II) (Saraji and Yousefi 2009) ions from aqueous solutions. The imprinted metal ions were completely removed by leaching with 1 M HNO_3 or 0.01 M EDTA in 0.5 M HNO_3. Compared with nonimprinted polymer particles, the IIP had higher selectivity for metal ions. New IIPs for selective sorption and separation of Cr(III) (Birlik et al. 2007), Fe(III) (Xie et al. 2012), Ru(III) (Godlewska-Zyłkiewicz et al. 2012), Nd(III) (Jiajia et al. 2009), and Au(III) (Ahamed et al. 2013) were synthesized. The IIPs for separation and preconcentration of UO_2^{2+} ions were obtained (Ahmadi et al. 2010, James et al. 2009). The applicability of IIP materials for the removal of emerging toxic pollutant uranium from uranium mining industry feed simulant solution is successfully demonstrated. An Al(III)-ionic imprinted polyamine functionalized silica gel sorbent was prepared by a surface imprinting technique for selectively adsorbing Al(III) from rare-earth solution (An et al. 2013). The adsorption of Th(IV) was studied using novel dibenzoylmethane MIPs, which was prepared using acryloyl-β-cyclodextrin as a monomer on surface-modified functional silica gel (Ji et al. 2013).

The Ni(II)-dimethylglyoxime (DMG)-IIP was encapsulated in polysulfone and electrospun into nanofibers with diameters ranging from 406 to 854 nm

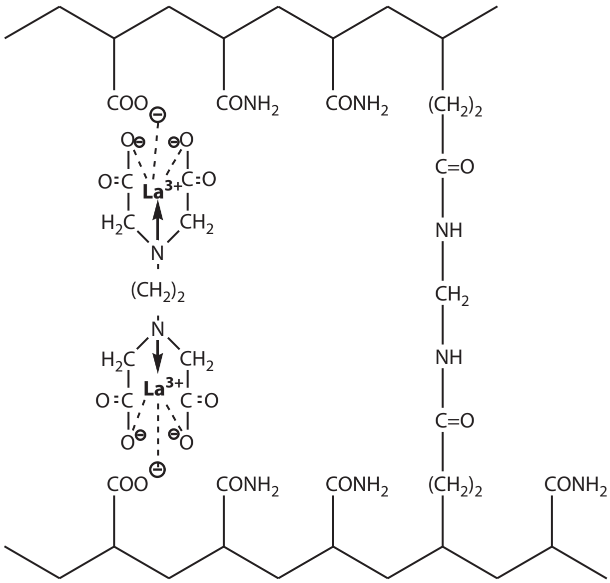


FIGURE 1.14 Scheme of immobilization of EDTA in AAm-AA hydrogel under *in situ* polymerization conditions.

(Rammika et al. 2011). The recovery of Ni(II) achieved using the Ni(II)-DMG imprinted nanofiber mats in water samples was found to range from 83% to 89%, while that of nonimprinted nanofiber mats was found to range from 59% to 65%, and that of polysulfone from 55% to 62%. The MIH was synthesized by immobilization of ethylenediaminetetraacetic acid–La(III) complex ([EDTA]:[La^{3+}] = 2:1 mol/mol) within AAm and AAc hydrogel matrix via *in situ* cross-linking polymerization (Bekturganov et al. 2010) (Figure 1.14).

It is expected that the EDTA–La(III) complex in hydrogel matrix is stabilized by electrostatic interaction between carboxylate anions and metal ions. After leaching out of La(III) ions by 0.1 N HCl, the MIH sample was used for recovery of trace concentration of rare-earth elements (REEs) from the real solution (Table 1.1).

Sorption of REE was also performed by commercially available Russian-made cation exchanger КУ-2-8н (Smirnov et al. 2002) (Table 1.2).

TABLE 1.1
Sorption of REE by MIH Sorbent from the Real Solution

	Initial Concentration of REE, mg/L							
Sorption	**La**	**Ce**	**Pr**	**Nd**	**Y**	**Dy**	**Gd**	**Total**
Stock solution	0.024	0.23	0.041	0.036	0.26	0.35	13.84	14.78
After sorption by MIH	0	0	0.04	$16 \cdot 10^{-3}$	0.028	$5 \cdot 10^{-4}$	13.17	13.25
Sorption degree, %	100	100	0	95.5	89.25	99.86	4.84	89.64

TABLE 1.2
Sorption of REE by КУ-2-8н Cation-Exchange Resin from the Real Solution

	Initial Concentration of REE, mg/L							
Sorption	**La**	**Ce**	**Pr**	**Nd**	**Y**	**Dy**	**Gd**	**Total**
Stock solution	—	0.46	0.065	0.061	0.23	0.20	6.54	7.556
After sorption by КУ-2-8н	—	0.29	0.065	0.021	0.032	0.13	4.75	5.291
Sorption degree, %	—	36.96	0	65.67	86.08	35.00	27.37	70.02

Comparison of the sorption effectiveness of REE by cation exchanger КУ-2-8н and MIH is in favor of the latter. Excepting for Pr and Gd, the EDTA-immobilized hydrogel sample adsorbs from 89% to 100% of REE during 20 min. Ammonium salt of EDTA was also used as an eluent in selective separation of REE (Lu, Sm, and Y) by ion-exchange resins based on iminodiacetic acid (Moore 2000). In spite of selective separation of REE by iminodiacetic resin in hydrogen form, the disadvantage of this process is the multistage character that consists of transferring of iminodiacetate resin at first to hydrogen form, then to ammonium form, saturation of iminodiacetate resin by REE solutions, and elution of REE by EDTA.

1.7 CONCLUDING REMARKS

Thus, the literature survey shows that the "smart" composite hydrogel materials are a fast developing and emerging field of polymer science. Synthetic and natural polymers including inorganic polymers, micro- and nanogels, metal nanoparticles, high- and low-molecular-weight ligands may be embedded into the hydrogel network, resulting in improvement of the mechanical properties and biocompatibility, making them as carriers for the controlled release of drugs and as catalysts, and providing stimuli-sensitive compositions. Structure, morphology, and physicochemical and physicomechanical properties of composite hydrogel materials are determined by both network structure and immobilized substances. The composite hydrogel materials can be applied in medicine, biotechnology, catalysis, environmental protection, and oil industry.

ABBREVIATIONS

AA	Allylamine
AAc	Acrylic acid
AAm	Acrylamide
AAm-AAc	Acrylamide and acrylic acid
AAm-SA	Poly(acrylamide-*co*-sodium acrylate)
AgNPs	Silver nanoparticles
AMPS	2-Acrylamido-2-methyl-1-propanesulfonic acid
ARPDs	Asphaltene–resin–paraffin depositions
AuNPs	Gold nanoparticles
BSA	Bovine serum albumin
CPAM	Cationic polyacrylamide

CTS	Chitosan
CTS-g-PAAc/MMT	Chitosan-*g*-poly(acrylic acid)/montmorillonite
Dex-MA	Methacrylated dextran
DLS	Dynamic light scattering
DMG	Dimethylglyoxime
EDTA	Ethylenediaminetetraacetic acid
FTIR	Fourier transform infrared spectroscopy
GE	Gelatin
IIP	Ion-imprinted polymers
IPN	Interpenetrating polymer network
MAA	Methacrylic acid
MB	Methylene blue
MBAA	Methylenebisacrylamide
MIH	Molecular imprinted hydrogels
MIP	Molecularly imprinted polymers
MIT	Molecular imprinted technology
MMT	Montmorillonite
MRT	Molecular recognition technology
NIPA	*N*-Isopropylacrylamide
NIPA-AAc	*N*-Isopropylacrylamide and acrylic acid
NIPA-IA	*N*-Isopropylacrylamide-itaconic acid
NIPA-HEMA	Poly(isopropylacrylamide-*co*-hydroxyethylmethacrylate)
PAAc-B-FeCo	Poly(acrylic acid)–bentonite–FeCo
PAAH	Poly(acrylamide) hydrogel
PdNPs	Palladium nanoparticles
PEI	Polyethyleneimine
PNIPA	Poly-*N*-isopropylacrylamide
PVP	Poly(*N*-vinyl-2-pyrrolidone)
PVP gel	Poly(*N*-vinyl-2-pyrrolidone)gel
PSA	Poly(sodium acrylate)
REE	Rare-earth elements
SA	Sodium alginate
SEM	Scanning electron microscopy
SS	Silk sericin
TON	Turnover numbers
VPTT	Volume-phase-transition temperature
w.r.	Weight ratio
XRD	X-ray diffraction

REFERENCES

Abdurrahmanoglu, S., V. Can, and O. Okay. 2008. Equilibrium swelling behavior and elastic properties of polymer–clay nanocomposite hydrogels. *J. Appl. Polym. Sci.* 109: 3714–3724.

Ahamed, M.E.H., X.Y. Mbianda, A.F. Mulaba-Bafubiandi, and L. Marjanovic. 2013. Selective extraction of gold(III) from metal chloride mixtures using ethylenediamine *N*-(2-(1-imidazolyl)ethyl) chitosan ion-imprinted polymer. *Hydrometallurgy* 140: 1–13.

Ahmadi, S.J., O. Noori-Kalkhoran, and S. Shirvani-Arani. 2010. Synthesis and characterization of new ion-imprinted polymer for separation and preconcentration of uranyl (UO_2^{2+}) ions. *J. Hazard. Mater.* 175: 193–197.

Akdemir, S. and N. Kayaman-Apohan. 2007. Investigation of swelling, drug release and diffusion behaviors of poly(*N*-isopropylacrylamide)/poly(*N*-vinylpyrrolidone) full-IPN hydrogels. *Polym. Adv. Technol.* 18: 932–939.

Ali, Sh.A. and Sh.A. Haladu. 2013. A novel cross-linked poly zwitterion/anion having pH-responsive carboxylate and sulfonate groups for the removal of Sr^{2+} from aqueous solution at low concentrations. *React. Funct. Polym.* 73: 796–804.

Ali, Sh.A. and O.Ch.S. Hamouz. 2012. Comparative solution properties of cyclocopolymers having cationic, anionic, zwitterionic and zwitterionic/anionic backbones of similar degree of polymerization. *Polymer* 53: 3368–3377.

Ali, Sh.A., O.Ch.S. Hamouz, and N.M. Hassan. 2013. Novel cross-linked polymers having pH-responsive amino acid residues for the removal of Cu^{2+} from aqueous solution at low concentrations. *J. Hazard. Mater.* 248–249: 47–58.

Al-Yaari, M. 2011. Paraffin wax deposition: Mitigation and removal techniques. *SPE Saudi Arabia Section Young Professionals Technical Symposium*, Dhahran, Saudi Arabia, March 14–16, 2011.

An, F., B. Gao, X. Huang, Y. Zhang, Y. Li, Y. Xu, Z. Zhang, J. Gao, and Z. Chen. 2013. Selectively removal of Al(III) from Pr(III) and Nd(III) rare earth solution using surface imprinted polymer. *React. Funct. Polym.*73: 60–65.

Anderson, N.J., B.A. Bolto, R.J. Eldridge, and M.B. Jackson. 1993. Polyampholyts for water treatment with magnetic particles. *React. Polym.*19: 87–95.

Andersson, L.I. and K. Mobach. 1990. Enantiomeric resolution on molecularly imprinted polymers prepared with only non-covalent and non-ionic interactions. *J. Chromatogr.* 516(2): 313–322.

Anil, K.A. 2007. Stimuli-induced pulsatile or triggered release delivery systems for bioactive compounds. Recent patents on endocrine. *Metab. Immun. Drug Discov.* 1: 83–90.

Anish, K.G. and W.S. Abdul. 2012. Environmental responsive hydrogels: A novel approach in drug delivery system. *J. Drug Deliv. Ther.* 2: 81–88.

Annenkov, V.V., E.N. Danilovtzeva, V.V. Saraev, and I.A. Alsarsur. 2000. Interaction of copolymer of acrylic acid and 1-vinylimidazole with copper(ll) ions in aqueous solution. *Izv. Russian Acad. Nauk Ser. Khim*. 12: 2047–2054.

Annenkov, V.V., E.N. Danilovtseva, V.V. Saraev, and A.I. Mikhaleva. 2003. Complexation of copper(II) ions with imidazole–carboxylic polymeric systems. *J. Polym. Sci.* 41: 2256–2263.

Arasawa, H., C. Odawara, R. Yokoyama, H. Saitoh, T. Yamauchi, and N. Tsubokawa. 2004. Grafting of zwitterion-type polymers on to silica gel surface and their properties. *React. Funct. Polym.* 61: 153–161.

Arica, M.Y., H.A. Öktem, Z. Öktem, and S.A. Tuncel. 1999. Immobilization of catalase in poly(isopropylacrylamide-*co*-hydroxyethylmethacrylate) thermally reversible hydrogels. *Polym. Int*. 48: 879–884.

Avvaru, N.R., N.R. de Tacconi, and K. Rajeshwar. 1998. Compositional analysis of organic-inorganic semiconductor composites. *Analyst* 123: 113–116.

Bajpai, A.K., S.K. Shukla, S. Bhanu, and S. Kankane. 2008. Responsive polymers in controlled drug delivery. *Prog. Polym. Sci.* 33: 1088–1118.

Balasubramanian, S.K., L. Yang, L.-Y.L. Yung, Ch.-N. Ong, W.-Y. Ong, and L.E. Yu. 2010. Characterization, purification, and stability of gold nanoparticles. *Biomaterials* 31(34): 9023–9030.

Behbahani, M., A. Bagheri, M. Taghizadeh, M. Salarian, O. Sadeghi, L. Adlnasab, and K. Jalali. 2013. Synthesis and characterisation of nano structure lead (II) ion-imprinted polymer as a new sorbent for selective extraction and preconcentration of ultra trace amounts of lead ions from vegetables, rice, and fish samples. *Food Chem.* 138: 2050–2056.

Bekturganov, N.S., N.K. Tusupbayev, S.E. Kudaibergenov, G.S. Tatykhanova, L.V. Semushkina, and Zh.E. Ibrayeva. 2010. Method of recovery of rare earth elements from solution. Innovation Patent of Kazakhstan No. 24563.

Bekturov, E.A. and S.E. Kudaibergenov. 1996. *Catalysis by Polymers.* Huthig & Wepf Verlag, Heidelberg, Germany, 153pp.

Bekturov, E.A., S.E. Kudaibergenov, R.M. Iskakov, A.K. Zharmagambetova, Zh.E. Ibraeva, and S. Shmakov. 2010. *Polymer-Protected Nanoparticles of Metals*. Print-S Almaty, 274pp. (in Russian).

Bekturov, E.A., S.E. Kudaibergenov, and V.B. Sigitov. 1986. Complexation of amphoteric copolymer of 2-methyl-5-vinylpyridine-acrylic acid with copper(II) ions and catalase like activity of polyampholyte-metal complexes. *Polymer* 27: 1269–1272.

Bergbreiter, D.E., B.L. Case, Y.-S. Liu, and J.W. Caraway. 1998. Poly(*N*-isopropylacrylamide) soluble polymer supports in catalysis and synthesis. *Macromolecules* 31: 6053–6062.

Bergmann, N.M. and A.P. Nicholas. 2008. Molecular imprinted polymers with specific recognition for macromolecules and proteins. *Prog. Polym. Sci.* 33(3): 271–288.

Bessbousse, H., J.-F. Verchere, and L. Lebrun. 2012. Characterisation of metal-complexing membranes prepared by the semi-interpenetrating polymer networks technique. Application to the removal of heavy metal ions from aqueous solutions. *Chem. Eng. J.* 187: 16–28.

Birlik, E., A. Ersoz, E. Acıkkalp, A. Denizli, and R. Say. 2007. Cr(III)-imprinted polymeric beads: Sorption and preconcentration studies. *J. Hazard. Mater.* 140: 110–116.

Buengera, D., F. Topuza, and J. Groll. 2012. Hydrogels in sensing applications. *Prog. Polym. Sci.* 37: 1678–1719.

Byrne, M.E., K. Park, and N.A. Peppas. 2002. Molecular imprinting within hydrogels. *Adv. Drug Deliv. Rev.* 54: 149–161.

Byrne, M.E. and V. Salian. 2008. Molecular imprinting within hydrogels II: Progress and analysis of the field. *Int. J. Pharm*. 364: 188–212.

Cameron, A., H.S. Andersson, L.I. Andersson, R.J. Ansell, N. Kirsch, I.A. Nicholls, J. O'Mahony, and M.J. Whitcombe. 2006. Molecular imprinting science and technology: A survey of the literature for the years up to and including 2003. *J. Mol. Recogn.* 19: 106–180.

Cândido, J., A.G.B. Pereira, A.R. Fajardo, M.P.S. Ricardo Nágila, P.A. Feitosa Judith, C.M. Edvani, and H.A.R. Francisco. 2013. Poly(acrylamide-*co*-acrylate)/rice husk ash hydrogel composites II. Temperature effect on rice husk ash obtention. *Compos. B Eng.* 51: 246–253.

Casoloro, M., F. Bignotti, L. Sartore, and M. Penco. 2001. The thermodynamics of basic and amphoteric poly(amidoamine)s containing peptide nitrogens as potential binding sites for metal ions. *Polymer* 42: 903–912.

Chan, W.C. and J.Y. Wu. 2001. Dynamic adsorption behaviors between Cu^{2+} ion and water-insoluble amphoteric starch in aqueous solutions. *J. Appl. Polym. Sci.* 81: 2849–2855.

Charles, O., S. Al Hamouz, and S.A. Ali. 2012. Removal of heavy metal ions using a novel cross-linked polyzwitterionic phosphonate. *Sep. Purif. Technol.* 98: 94–101.

Chauhan, G.S., B. Singh, and S. Kumar. 2005. Synthesis and characterization of *N*-vinyl pyrrolidone and cellulosics based functional graft copolymers for use as metal ions and ions and iodine sorbents. *J. Appl. Polym. Sci.* 98: 373–382.

Chauhan, K., G.S. Chauhan, and J.H. Ahn. 2009. Synthesis and characterization of novel guar gum hydrogels and their use as Cu^{2+} sorbents. *J. Biotech*. 100: 3599–3603.

Chen, H., D.M. Lentz, and R.C. Hedden. 2012a. Solution templating of Au and Ag nanoparticles by linear poly[2-(diethylamino)ethyl methacrylate]. *J. Nanopart. Res*. 14: 690–698.

Chen, H. and A. Wang. 2009. Adsorption characteristics of Cu(II) from aqueous solution onto poly(acrylamide)/attapulgite composite. *J. Hazard. Mater.* 165: 223–231.

Chen, S., H. Zhong, B. Gu, Y. Wang, X. Li, Zh. Cheng, L. Zhang, and Ch. Yao. 2012b. Thermosensitive phase behavior and drug release of in situ *N*-isopropylacrylamide copolymer. *Mater. Sci. Eng.* 32: 2199–2204.

Cheng, Y.-J., S. Zhou, and J.S. Gutmann. 2007. Morphology transition in ultrathin titania films: From pores to lamellae. *Macromol. Rapid Commun.* 28: 1392–1396.
Cho, E.Ch., J. Kim, A. Fernández-Nieves, and D.A. Weitz. 2008. Highly responsive hydrogel scaffolds formed by three-dimensional organization of microgel nanoparticles. *Nanoletters* 8: 168–172.
Chung, J.W., Y. Guo, S.-Y. Kwak, and R.D. Priestley. 2012. Understanding and controlling gold nanoparticle formation from a robust self-assembled cyclodextrin solid template. *J. Mater. Chem*. 22: 6017–6026.
Ciferri, A. and S.E. Kudaibergenov. 2007. Natural and synthetic polyampholytes. I. Theory and basic structures. *Makromol. Rapid Commun.* 28: 1953–1968.
Coughlan, D.C., F.P. Quilty, and O.I. Corrigan. 2004. Effect of drug physiochemical properties on swelling/deswelling kinetics and pulsatile drug release from thermoresponsive poly(*N*-isopropylacrylamide) hydrogels. *J. Control. Release* 98: 97–114.
Dai, J., P. Yao, N. Hua, P. Yang, and Y. Du. 2007. Preparation and characterization of polymer-protected Pt-Pt/Au core-shell nanoparticles. *J. Dispersion Sci. Technol*. 28: 872–875.
Dalaran, M., S. Emik, G. Güçlü, T.B. İyim, and S. Özgümüş. 2011. Study on a novel polyampholyte nanocomposite superabsorbent hydrogels: Synthesis, characterization and investigation of removal of indigo carmine from aqueous solution. *Desalination* 279: 170–182.
Dinu, M.V., M. Pradny, E.S. Dragan, and J. Michalek. 2013. Morphological and swelling properties of porous hydrogels based on poly(hydroxyethyl methacrylate) and chitosan modulated by ice-templating process and porogen leaching. *J. Polym. Res.* 20: 285.
Dolya, N., O. Rojas, S. Kosmella, B. Tiersch, J. Koetz, and S. Kudaibergenov. 2013. "One-pot" in situ formation of gold nanoparticles within poly(acrylamide) hydrogels. *Macromol. Chem. Phys*. 214: 114–121.
Dolya, N.A. 2009. Physico-chemical and catalytic properties of polymer-protected and gel-immobilized metals nanoparticles. PhD thesis, A. Bekturov Institute of Chemical Sciences, Almaty, Kazakhstan.
Dolya, N.A., Zh.E. Ibrayeva, E.A. Bekturov, and S.E. Kudaibergenov. 2009. Preparation, properties and catalytic activity of polymer-protected and gel-immobilized nanoparticles of gold, silver and palladium. *Bull. Natl. Acad. Sci. Republic of Kazakhstan* 4: 30–35.
Dolya, N.A., B.Kh. Musabayeva, M.G. Yashkrova, and S.E. Kudaibergenov. 2008a. Preparation, properties and catalytic activity of palladium nanoparticles immobilized within poly-*N*-isopropylacrylamide hydrogel matrix. *Chem. J. Kazakhstan* 1: 139–146.
Dolya, N.A., A.K. Zharmagambetova, B.Kh. Musabayeva, and S.E. Kudaibergenov. 2008b. Immobilization of polyethyleneimine-$[PdCl_4]^{-2}$ complexes into the matrix of polyacrylamide hydrogels and study of hydrogenation of allyl alcohol with the help of gel-immobilized nanocatalyst. *Bull. Natl. Acad. Sci. Republic of Kazakhstan* 1: 55–59.
Dorris, A., S. Rucareanu, L. Reven, C.J. Barrett, and R. Bruce Lennox. 2008. Preparation and characterization of polyelectrolyte-coated gold nanoparticles. *Langmuir* 24(6): 2532–2538.
Dragan, E.S. and D.F. Apopei Loghin. 2013. Enhanced sorption of Methylene Blue from aqueous solutions by semi-IPN composite cryogels with anionically modified potato starch entrapped in PAAm matrix. *Chem. Eng. J.* 234: 211–222.
Dragan, E.S. and M.V. Dinu. 2013. Design, synthesis and interaction with Cu^{2+} ions of ice templated composite hydrogels. *Res. J. Chem. Environ.* 17: 4–10.
Dunkin, I.R., J. Lenfeld, and D.C. Sherrington. 1993. Molecular imprinting of flat polycondensed aromatic-molecules in macroporous polymers. *Polymer* 34: 77–84.
Echeverria, C. and C. Mijangos. 2010. Effect of gold nanoparticles on the thermosensitivity, morphology, and optical properties of poly(acrylamide–acrylic acid) microgels. *Macromol. Rapid Commun.* 31: 54–58.
Eros, I., I. Csoka, E. Csanyi, and T.T. Wormsdorff. 2003. Examination of drug release from hydrogels. *Polym. Adv. Technol.* 14: 847–853.

Essawy, H. 2008. Poly(methyl methacrylate)-kaolinite nanocomposites prepared by interfacial polymerization with redox initiator system. *Colloid Polym. Sci.* 286: 795–803.

Fan, H.-T., J. Li, Z.-C. Li, and T. Sun. 2012. An ion-imprinted amino-functionalized silica gel sorbent prepared by hydrothermal assisted surface imprinting technique for selective removal of cadmium (II) from aqueous solution. *Appl. Surf. Sci.* 258: 3815–3822.

Feng, Q., F. Li, Q. Yan, Y.-C. Zhu, and C.-C. Ge. 2010. Frontal polymerization synthesis and drug delivery behavior of thermo-responsive poly(*N*-isopropylacrylamide) hydrogel. *Colloid Polym. Sci*. 288: 915–921.

Frimpong, R.A., S. Fraser, and J.Z. Hilt. 2006. Synthesis and temperature response analysis of magnetic-hydrogel nanocomposites. *J. Biomed. Mater. Res*. 80: 1–6.

Galaev, I.Y. and B. Mattiasson. 1999. 'Smart' polymers and what they could do in biotechnology and medicine. *Trends Biotechnol.* 17: 335–340.

Ge, F., M.-M. Li, H. Ye, and B.-X. Zhao. 2012. Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymer-modified magnetic nanoparticles. *J. Hazard. Mater.* 211–212: 366–372.

Godlewska-Żyłkiewicz, B., E. Zambrzycka, B. Leśniewska, and A.Z. Wilczewska. 2012. Separation of ruthenium from environmental samples on polymeric sorbent based on imprinted Ru(III)-allyl acetoacetate complex. *Talanta* 89: 352–359.

Gong, J.P., Y. Katsuyama, T. Kurokawa, and Y. Osada. 2003. Double-network hydrogels with extremely high mechanical strength. *Adv. Mater.* 15: 1155–1158.

Gorner, T., R. Gref, D. Michenot, F. Sommerb, M.N. Tranc, and E. Dellacherie. 1999. Lidocaine-loaded biodegradable nanospheres. Optimization of the drug incorporation into the polymer matrix. *J. Control. Release* 57: 259–268.

Hagiwara, H., Y. Shimizu, T. Hoshi, T. Suzuki, M. Ando, K. Ohkubo, and C. Yokoyama. 2001. Heterogeneous Heck reaction catalyzed by Pd/C in ionic liquid. *Tetrahedron Lett.* 42: 4349–4351.

Haraguchi, K., R. Farnworth, A. Ohbayashi, and T. Takehisa. 2003. Compositional effects on mechanical properties of nanocomposite hydrogels composed of poly(*N*,*N*-dimethylacrylamide) and clay. *Macromolecules* 36: 5732–5741.

Haraguchi, K. and H.J. Li. 2006. Mechanical properties and structure of polymer-clay nanocomposite gels with high clay content. *Macromolecules* 39: 1898–1905.

Haraguchi, K., K. Murata, and T. Takehisa. 2013. Stimuli-responsive properties of nanocomposite gels comprising (2-methoxyethylacrylate-*co*-*N*,*N*-dimethylacrylamide) copolymer-clay networks. *Macromol. Symp.* 329: 150–161.

Haraguchi, K. and T. Takehisa. 2002. Nanocomposite hydrogels: A unique organic–inorganic network structure with extraordinary mechanical, optical, and swelling/deswelling properties. *Adv. Mater.* 14: 1120–1124.

Haraguchi, K., T. Takehisa, and S. Fan. 2002. Effects of clay content on the properties of nanocomposite hydrogels composed of poly(*N*-isopropylacrylamide) and clay. *Macromolecules* 35: 10162–10171.

Haruta, M. 1997. Novel catalysis of gold deposited on metal oxides. *Catal. Surveys Japan* 1: 61–73.

Haruta, M. and M. Daté. 2001. Advances in the catalysis of Au nanoparticles (review). *Appl. Catal. A: General* 222: 427–437.

Hendrickson, O.D., A.V. Zherdev, and B.B. Dzantiyev. 2006. Molecularly imprinted polymers and their application in biochemical analysis. *Achievements Biol. Chem.* 46: 149–192.

Hoare, T.R. and D.S. Kohane 2008. Hydrogels in drug delivery: Progress and challenges. *Polymer* 49: 1993–2007.

Hoffman, A. and P.S. Stayton. 2004. Bioconjugates of smart polymers and proteins: Synthesis and application. *Macromol. Symp.* 207: 139–151.

Holgado, M.A., J.L. Arias, M.J. Cózar, J. Alvarez-Fuentes, A.M. Gañán-Calvo, and M. Fernández-Arévalo. 2008. Synthesis of lidocaine-loaded PLGA microparticles by flow focusing: Effects on drug loading and release properties. *Int. J. Pharm.* 358: 27–35.

Holtz, J.H. and S.A. Asher. 1997. Polymerized colloidal crystal hydrogel films as intelligent chemical sensing materials. *Nature* 389: 829–832.

Hoppe, C.E., M. Lazzari, I. Pardiñas-Blanco, and M.A. López-Quintela. 2006. One-step synthesis of gold and silver hydrosols using poly(*N*-vinyl-2-pyrrolidone) as a reducing agent. *Langmuir* 22: 7027–7034.

Ibrayeva, Zh.E. 2010. Composite polymer hydrogels. *Chem. J. Kazakhstan* 2: 165–175.

Ibrayeva, Zh.E., S.E. Kudaibergenov, and E.A. Bekturov. 2013. *Stabilization of Metal Nanoparticles by Hydrophilic Polymers* (in Russian). LAP Lambert Academic Publishing, Saarbrücken, Germany, 376pp.

Isobe, N., D. Lee, Y. Kwon, S. Kimura, Sh. Kuga, M. Wada, and U. Kim. 2011. Immobilization of protein on cellulose hydrogel. *Cellulose* 18: 1251–1256.

Jaggard, W.S. and A. Allen. 1977. Gel-like composition for use as a pig in a pipeline, US Patent No. 4003393.

Jagur-Grodzinski, J. 2010. Polymeric gels and hydrogels for biomedical and pharmaceutical applications. *Polym. Adv. Technol.* 21: 27–47.

James, D., G. Venkateswaran, and T. Prasada Rao. 2009. Removal of uranium from mining industry feed simulant solutions using trapped amidoxime functionality within a mesoporous imprinted polymer material. *Microporous Mesoporous Mater*. 119: 165–170.

Ji, X.Z., H.J. Liu, L.L. Wang, Y.K. Sun, and Y.W. Wu. 2013. Study on adsorption of Th(IV) using surface modified dibenzoylmethane molecular imprinted polymer. *J. Radioanal. Nucl. Chem*. 295: 265–270.

Jia, X., Y. Lia, B. Zhanga, Q. Chenga, and Sh. Zhanga. 2008. Preparation of poly(vinyl alcohol)/kaolinite nanocomposites via in situ polymerization. *Mater. Res. Bull*. 43: 611–617.

Jiajia G., C. Jibao, and S. Qingde. 2009. Ion imprinted polymer particles of neodymium: Synthesis, characterization and selective recognition. *J. Rare Earths* 27: 22.

Jiang, B. and Y. Zhang. 1993. Immobilization of catalase on crosslinked polymeric hydrogels-effect of anion on the activity of immobilized enzyme. *Eur. Polym. J.* 29: 1251–1254.

Jiang, H.Q., S. Manolache, A.C.L. Wong, and F.S. Denes. 2004. Plasma-enhanced deposition of silver nanoparticles onto polymer and metal surfaces for the generation of antimicrobial characteristics. *J. Appl. Polym. Sci*. 93: 1411–1422.

Jiang, W. and K. Irgum. 1999. Covalently bonded polymeric zwitterionic stationary phase for simultaneous separation of inorganic cations and anions. *Anal. Chem*. 71: 333–344.

Kabanov, V.A., A.A. Efendiev, and D.D. Orujev. 1977. Obtaining of complex-forming polymer sorbent with location of macromolecules "tuned" to the sorbed ion. *Vysokomol. Soedin. Ser. B* 19: 91–92.

Kabanov, V.A., A.A. Efendiev, and D.D. Orujev. 1979. Complex-forming polymeric sorbents with macromolecular arrangement favorable for ion sorption. *J. Appl. Polym. Sci.* 24: 259–267.

Kabiri, K. and M.J. Zohuriaan-Mehr. 2003. Superabsorbent hydrogel composites. *Polym. Adv. Technol.* 14: 438–444.

Kalfus, J., N. Singh, and A.J. Lesser. 2012. Reinforcement in nano-filled PAA hydrogels. *Polymer* 53: 2544–2547.

Kevadiya, B.D., G.V. Joshi, H.M. Mody, and H.C. Bajaj. 2011. Biopolymer–clay hydrogel composites as drug carrier: Host–guest intercalation and in vitro release study of lidocaine hydrochloride. *Appl. Clay Sci*. 52: 364–367.

Khvan, A.M., V.V. Chupov, O.V. Noa, and N.A. Plate. 1985. Experimental study of intramolecular crosslinking of poly-*N*-methacryloyl-L-lysine by copper(II) ions. *Vysokomol. Soedin. Ser. A* 27: 1243–1248.

Kidambi, S., J.H. Dai, J. Li, and M.L. Bruening. 2004. Selective hydrogenation by Pd nanoparticles embedded in polyelectrolyte multilayers. *J. Am. Chem. Soc.* 126: 2658–2659.

Kim, J.-H. and T.R. Lee. 2007. Hydrogel-templated growth of large gold nanoparticles: Synthesis of thermally responsive hydrogel-nanoparticle composites. *Langmuir* 23: 6504–6509.

Kirsch, N., C. Alexander, M. Lubke, M.J. Whitcombe, and E.N. Vulfson. 2000. Enhancement of selectivity of imprinted polymers via post-imprinting modification of recognition sites. *Polymer* 41: 5583–5590.

Klinger, D. and K. Landfester. 2012. Stimuli-responsive microgels for the loading and release of functional compounds: Fundamental concepts and applications. *Polymer* 53: 5209–5231.

Kohler, K., R.G. Heidenreich, J.G.E. Krauter, and M. Pietsch. 2001. Highly active palladium/activated carbon catalysts for heck reactions: Correlation of activity, catalyst properties, and Pd leaching. *Chem. Eur. J.* 8: 622–631.

Kowalczyk, M., Z. Hubicki, and D. Kołodynska. 2013. Modern hybrid sorbents—New ways of heavy metal removal from waters. *Chem. Eng. Proc.* 70: 55–65.

Kudaibergenov, S.E. 2002. *Polyampholytes: Synthesis, Characterization and Application*. Kluwer Academic/Plenum Publishers, New York, 220pp.

Kudaibergenov, S.E. 2008. Polyampholytes. In: *Encyclopedia of Polymer Material and Technology*. John Wiley & Sons. Inc., pp. 1–30.

Kudaibergenov, S.E., Zh. Adilov, D. Berillo, G. Tatykhanova, Zh. Sadakbaeva, Kh. Abdullin, and I. Galaev. 2012b. Novel macroporous amphoteric gels: Preparation and characterization. *Express Polym. Lett.* 6: 346–353.

Kudaibergenov, S.E., L.A. Bimendina, and M.G. Yashkarova. 2007. Preparation and characterization of novel polymeric betaines based on aminocrotonates. *J. Macromol. Sci. A: Pure Appl. Chem.* 44: 899–912.

Kudaibergenov, S.E. and A. Ciferri. 2007. Natural and synthetic polyampholytes, functions and applications. *Makromol. Rapid. Commun.* 28: 1969–1986.

Kudaibergenov, S.E., N. Dolya, G. Tatykhanova, Zh. Ibrayeva, B. Musabayeva, M. Yashkarova, and L. Bimendina. 2007. Semi-interpenetrating polymer networks of polyelectrolytes. *Eurasian Chem. Technol. J.* 9: 177–192.

Kudaibergenov, S.E., Zh.E. Ibraeva, N.A. Dolya, B.Kh. Musabayeva, A.K. Zharmagambetova, and J. Koetz. 2008. Semi-interpenetrating hydrogels of polyelectrolytes, polymer-metal complexes and polymer-protected palladium nanoparticles. *Macromol. Symp.* 274: 11–21.

Kudaibergenov, S.E., W. Jaeger, and A. Laschewsky. 2006. Polymeric betaines: Synthesis, characterization and application. *Adv. Polym. Sci.* 201: 157–224.

Kudaibergenov, S.E., N. Nueraje, and V. Khutoryanskiy. 2012a. Amphoteric nano-, micro-, and macrogels, membranes, and thin films. *Soft Matter* 8: 9302–9321.

Kudaibergenov, S.E., G. Tatykhanova, and Zh. Ibraeva. 2011. Immobilization and controlled release of bioactive substances from stimuli-responsive hydrogels. *Biodefence.* NATO Science for Peace and Security Series-A: Chemistry and Biology. Springer, Dordrecht, The Netherlands, Chapter 19, pp. 79–188.

Kumar, A., A. Srivastava, I. Galaev, and B. Mattiasson. 2007. Smart polymers: Physical forms and bioengineering applications. *Prog. Polym. Sci.* 32: 1205–1237.

Kundakci, S., Ö.B. Üzüm, and E. Karadağ. 2008. Swelling and dye sorption studies of acrylamide/2-acrylamido-2-methyl-1-propanesulfonic acid/bentonite highly swollen composite hydrogels. *React. Funct. Polym.* 68: 458–473.

Kurokawa, Y. and M. Sasaki. 1982. Complexation between polyions and hydrous inorganic oxides and adsorption properties of complex. *Makromol. Chem.* 183: 679–685.

Lao, L.L. and R.V. Ramanujan. 2004. Magnetic and hydrogel composite materials for hyperthermia applications. *J. Mater. Sci. Mater. Med.* 15: 1061–1064.

Lázaro Martínez, J.M., M.F. Leal Denis, V. Campo Dall'Orto, and G.Y. Buldain. 2008a. Synthesis, FTIR, solid-state NMR and SEM studies of novel polyampholytes or polyelectrolytes obtained from EGDE, MAA and imidazoles. *Eur. Polym. J.* 44: 392–407.

Lázaro Martínez, J.M., M.F. Leal Denis, L.L. Piehl, E. Rubín de Celis, G.Y. Buldain, and V.C. Dall'Orto. 2008b. Studies on the activation of hydrogen peroxide for color removal in the presence of a new Cu(II)-polyampholyte heterogeneous catalyst. *Appl. Catal. Environ.* 82: 273–283.

Lázaro Martínez, J.M., E. Rodríguez-Castellón, R.M. Torres Sánchez, L.R. Denaday, G.Y. Buldain, and V.C. Dall'Orto. 2011. XPS studies on the Cu(I,II)–polyampholyte heterogeneous catalyst: An insight into its structure and mechanism. *J. Mol. Catal*. 339: 43–51.

Leadbeater, N.E. and M. Marco. 2002. Ligand-free palladium catalysis of the Suzuki reaction in water using microwave heating. *Org. Lett*. 4(17): 2973–2976.

Lee, K.Y. and S.H. Yuk. 2007. Polymeric protein delivery systems. *Prog. Polym. Sci.* 32: 669–697.

Lee, W.F. and L.G. Yang. 2004. Superabsorbent polymeric materials. XII. Effect of montmorillonite on water absorbency for poly(sodium acrylate) and montmorillonite nanocomposite superabsorbents. *J. Appl. Polym. Sci.* 92: 3422–3429.

Lee, Y.-J. and P.V. Braun. 2003. Tunable inverse opal hydrogel pH sensors. *Adv. Mater.* 15: 563–566.

Li, Q., H. Liua, T. Liu, M. Guo, B. Qinga, X. Ye, and Z. Wu. 2010. Strontium and calcium ion adsorption by molecularly imprinted hybrid gel. *Chem. Eng. J.* 157: 401–407.

Li, S., Y. Wu, J. Wang, Q. Zhang, Y. Kou, and S. Zhang. 2010. Double-responsive polyampholyte as a nanoparticle stabilizer: Application to reversible dispersion of gold nanoparticles. *J. Mater. Chem*. 20: 4379–4384.

Li, Z.-C., H.-T. Fan, Yi. Zhang, M.-X. Chen, Z.-Y. Yu, X.-Q. Cao, and T. Sun. 2011. Cd(II)-imprinted polymer sorbents prepared by combination of surface imprinting technique with hydrothermal assisted sol–gel process for selective removal of cadmium(II) from aqueous solution. *Chem. Eng. J.* 171: 703–710.

Lianga, R. and M. Liu. 2007. Preparation of poly(acrylic acid-*co*-acrylamide)/kaolin and release kinetics of urea from it. *J. Appl. Polym. Sci.* 106: 3007–3015.

Lianga, R., M. Liu, and L. Wu. 2007. Controlled release NPK compound fertilizer with the function of water retention. *React. Funct. Polym.* 67: 769–779.

Lin, J., J. Wu, Z. Yang, and M. Pu. 2001. Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. *Macromol. Rapid Commun.* 22: 422–424.

Liu, D.Z., M.T. Sheu, C. Chen, Y.R. Yang, and H.O. Ho 2007. Release characteristics of lidocaine from local implant of polyanionic and polycationic hydrogels. *J. Control. Release* 118: 333–339.

Liusheng, Z., B. Brittany, and A. Frank. 2011. Stimuli responsive nanogels for drug delivery. *Soft Matter* 7: 5908–5916.

Lombardo Lupano, L.V., J.M. Lázaro Martínez, L.L. Piehl, E.R. de Celis, and V. Campo Dall'Orto. 2013. Activation of H_2O_2 and superoxide production using a novel cobalt complex based on a polyampholyte. *Appl. Catal. General* 467: 342–354.

Lu, F., J. Ruiz, and D. Astruc. 2004. Palladium-dodecanethiolate nanoparticles as stable and recyclable catalysts for the Suzuki-Miyaura reaction of aryl halides under ambient conditions. *Tetrahedron Lett*. 45: 9443–9445.

Lu, Zh., G. Liu, and S. Duncan. 2003. Poly(2-hydroxyethyl acrylate-*co*-methyl acrylate)/SiO_2/TiO_2 hybrid membranes. *J. Membr. Sci.* 221: 113–122.

Mahltig, B., N. Cheval, J.-F. Gohy, and A. Fahmi. 2010. Preparation of gold nanoparticles under presence of the diblock polyampholyte PMAA-b-PDMAEMA. *J. Polym. Res*. 17: 579–588.

Makysh, G.Sh., L.A. Bimendina, and S.E. Kudaibergenov. 2002. Interaction of richlocaine with some linear and crosslinked polymers. *Polymer* 43: 4349–4353.

Makysh, G.Sh., L.A. Bimendina, K.B. Murzagulova, and S.E. Kudaibergenov. 2003. Interaction of a new anesthetic drug richlocain with linear and weakly crosslinked poly-*n*-vinylpyrrolidone. *J. Appl. Polym. Sci.* 89: 2977–2981.

Manpreet, K., Rajnibala, and A. Sandeep. 2013. Stimuli responsive polymers and their applications in drug delivery. *Int. J. Adv. Pharm. Sci.* 4: 477–495.

Marcin, K., J. Romanski, K. Michniewicz, J. Jurczak, and Z. Stojek. 2010. Influence of polymer network-metal ion complexation on the swelling behaviour of new gels with incorporated α-amino acid groups. *Soft Matter* 6: 1336–1342.

Martínez, J.M.L., A.K. Chattah, G.A. Monti, M.F.L. Denis, G.Y. Buldain, and V. Campo Dall' Orto. 2008. New copper(II) complexes of polyampholyte and polyelectrolyte polymers: Solid-state NMR, FTIR, XRPD and thermal analyses. *Polymer*. 49: 5482–5489.

Martínez-Martínez, D., C. López-Cartes, A. Fernández, and J.C. Sánchez-López. 2008. Comparative performance of nanocomposite coatings of TiC or TiN dispersed in a-C matrixes. *Surf. Coat. Technol.* 203: 756–760.

Mattiasson, B., A. Kumar, and I. Yu Galaev. 2010. *Macroporous Polymers: Applications, Production, Properties and Biotechnological/Biomedical Applications*. CRC Press, Boca Raton, FL, 513pp.

Mayes, A.G. and M.J. Whitcombe. 2005. Synthetic strategies for the generation of molecularly imprinted organic polymers. *Adv. Drug Deliv. Rev*. 57: 1742–1778.

Metin, O., S. Sahin, and S. Ozkar. 2009. Water-soluble poly(4-styrenesulfonic acid-*co*-maleic acid) stabilized ruthenium(0) and palladium(0) nanoclusters as highly active catalysts in hydrogen generation from the hydrolysis of ammonia-borane. *Int. J. Hydrogen Energy* 34: 6304–6313.

Milasinovic, N., M.K. Krusic, Z. Knezevic-Jugovic, and J. Filipovic. 2010. Hydrogels of *N*-isopropylacrylamide copolymers with controlled release of a model protein. *Int. J. Pharm.* 383: 53–61.

Moore, B.M. 2000. Selective separation of rare earth elements by ion exchange in an iminodiacetic resin, US Patent No. 6093376.

Morrow, B.J., E. Matijević, and D.V. Goia. 2009. Preparation and stabilization of monodisperse colloidal gold by reduction with aminodextran. *J. Colloid Interface Sci*. 335: 62–69.

Mosbach, K. and O. Ramstrom. 1996. The emerging technique of molecular imprinting and its future impact on biotechnology. *J. Biotechnol.* 14: 163–170.

Motoyuki, I. and K. Hidehiro. 2009. Surface modification for improving the stability of nanoparticles in liquid media. *Kona Powder Part. J.* 27: 119–129.

Nakamura, T. and M. Ogawa. 2013. Adsorption of cationic dyes within spherical particles of poly(*N*-isopropylacrylamide) hydrogel containing smectite. *Appl. Clay Sci.* 83–84: 469–473.

Nakayama, A., A. Kakugo, J.P. Gong, Y. Osada, M. Takai, T. Erata, and S. Kawano. 2004. High mechanical strength double-network hydrogel with bacterial cellulose. *Adv. Funct. Mater.* 14: 1124–1128.

Nicholls, I.A., O. Ramstrom, and K. Mosbach. 1995. Insights into the role of the hydrogen-bond and hydrophobic effect on recognition in molecularly imprinted polymer synthetic peptide receptor mimics. *J. Chromatogr*. 691: 349–353.

Nishide, H., J. Deguchi, and E. Tsuchida. 1976. Selective adsorption of metal-ions on cross-linked poly(vinylpyridine) resin prepared with a metal-ion as a template. *Chem. Lett*. 5: 169–174.

Note, C., J. Koetz, L. Wattebled, and A. Laschewsky. 2007. Effect of a new hydrophobically modified polyampholyte on the formation of inverse microemulsions and the preparation of gold nanoparticles. *J. Colloid Interface Sci*. 308: 162–169.

Orozco-Guareño, E., F. Santiago-Gutiérrez, J.L. Morán-Quiroz, S.L. Hernandez-Olmos, V. Soto, W. de la Cruz, R. Manríquez, and S. Gomez-Salazar. 2010. Removal of Cu(II) ions from aqueous streams using poly(acrylic acid-co-acrylamide) hydrogels. *J. Colloid Interface Sci.* 349: 583–593.

Panic, V.V., Z.P. Madzarevic, T. Volkov-Husovic, and S.J. Velickovic. 2013. Poly(methacrylic acid) based hydrogels as sorbents for removal of cationic dye basic yellow 28: Kinetics, equilibrium study and image analysis. *Chem. Eng. J*. 217: 192–204.

Pardo-Yissar, V., R. Gabai, A.N. Shipway, T. Bourenko, and I. Willner. 2001. Gold nanoparticle/hydrogel composites with solvent-switchable electronic properties. *Adv. Mater*. 13: 1320–1323.

Park, T.G. 1993. Stabilization of enzyme immobilized in temperature-sensitive hydrogels. *Biotechol. Lett.* 15: 57–60.

Pavlyuchenko, V.N. and S.S. Ivanchev. 2009. Composite polymer hydrogels. *Vysokomol. Soedin. Ser. A* 51: 1075–1095.
Peppas, N.A., J.Z. Hilt, A. Khademhosseini, and R. Langer. 2006. Hydrogels in biology and medicine: From molecular principles to bionanotechnology. *Adv. Mater*. 18: 1345–1360.
Phan, N.T.S., D.H. Brown, and P. Styring. 2004. A polymer-supported salen-type palladium complex as a catalyst for the Suzuki-Miyaura cross-coupling reaction. *Tetrahedron Lett.* 45: 7915–7919.
Polakovič, M., T. Görner, R. Gref, and E. Dellacherie.1999. Lidocaine loaded biodegradable nanospheres: II. Modelling of drug release. *J. Control. Release* 60: 169–177.
Polyakov, M.V. 1931. Adsorption properties and structure of silica gel. *Zh. Fiz. Khim.* 2: 799–805.
Popa, M., N. Bajan, A.A. Popa, and A. Verestiuc. 2006. The preparation, characterization and properties of catalase immobilized on crosslinked gellan. *J. Macromol. Sci. A: Pure Appl. Chem.* 43: 355–367.
Qiu, Y. and K. Park. 2012. Environment-sensitive hydrogels for drug delivery. *Adv. Drug Deliv. Rev.* 64: 49–60.
Ram, S., L. Agrawal, A. Mishra, and S.K. Roy. 2011. Synthesis and optical properties of surface stabilized gold nanoparticles with poly(*N*-vinylpyrrolidone). Polymer molecules of a nanofluid. *Adv. Sci. Lett.* 4: 3431–3438.
Rammika, M., G. Darko, and N. Torto. 2011. Incorporation of Ni(II)-dimethylglyoxime ion-imprinted polymer into electrospun polysulphone nanofibre for the determination of Ni(II) ions from aqueous samples. *Water SA* 37: 539–546.
Ray, S.S. and M. Okamoto. 2003. Polymer/layered silicate nanocomposite: A review from preparation to processing. *Prog. Polym. Sci.* 28: 1539–1641.
Rivas, B.L., S. Villegas, and B. Ruf. 2006. Water-insoluble polymers containing amine, sulfonic acid, and carboxylic acid groups: Synthesis, characterization, and metal-ion-retention properties. *J. Appl. Polym. Sci.* 99: 3266–3274.
Romana, S., R.K. Ning, and N.Z. Richard. 2012. Surface-imprinted polymers in microfluidic devices. *Sci. China Chem.* 55: 469–483.
Rutkevičius, M., S.K. Munusami, Z. Watson, A.D. Field, M. Salt, S.D. Stoyanov, J. Petkov, G.H. Mehl, and V.N. Paunov. 2012. Fabrication of novel lightweight composites by a hydrogel templating technique. *Mater. Res. Bull.* 47: 980–986.
Rychkov, V.N. 2003. Uranium sorption from sulfate solutions with polyampholytes. *Radiochemistry* (in Russian) 45: 56–60.
Rzaev, Z.M., S. Dinçer, and E. Pişkin. 2007. Functional copolymers of *N*-isopropylacrylamide for bioengineering applications. *Prog. Polym. Sci.* 32: 534–595.
Saber-Samandari, S. and M. Gazi. 2013. Cellulose-graft-polyacrylamide/hydroxyapatite composite hydrogel with possible application in removal of Cu (II) ions. *React. Funct. Polym*. 73: 1523–1530.
Sahiner, N. 2004. In situ metal particle preparation in cross-linked poly(2-acrylamido-2-methyl-1-propansulfonic acid) hydrogel networks. *Colloid Polym. Sci.* 285: 283–292.
Sahiner, N. 2013. Soft and flexible hydrogel templates of different sizes and various functionalities for metal nanoparticle preparation and their use in catalysis. *Prog. Polym. Sci.* 38: 1329–1356.
Saraji, M. and H. Yousefi. 2009. Selective solid-phase extraction of Ni(II) by an ion-imprinted polymer from water samples. *J. Hazard. Mater*. 167: 1152–1157.
Sellergren, B. 1997. Noncovalent molecular imprinting: Antibody-like molecular recognition in polymeric network materials. *Trends Anal. Chem.* 16: 310–320.
Sellergren, B., B. Ekberg, and K. Mosbach. 1985. Molecular imprinting of amino acid derivatives in macroporous polymers. Demonstration of substrate and enantioselectivity by chromatographic resolution of racemic mixtures of amino acid derivatives. *J. Chromatogr. A* 347: 1–10.

Sershen, S.R., G.A. Mensing, M. Ng, N.J. Halas, D.J. Beebe, and J.L. West. 2005. Independent optical control of microfluidic valves formed from optomechanically responsive nanocomposite hydrogels. *Adv. Mater.* 17: 1366–1368.

Sershen, S.R., S.L. Westcott, N.J. Halas, and J.L. West. 2000. Temperature-sensitive polymer–nanoshell composites for photothermally modulated drug delivery. *J. Biomed. Mater. Res.* 51: 293–298.

Sershen, S.R., S.L. Westcott, J.L. West, and N.J. Halas. 2001. Anopto-mechanical nanoshell-polymer composite. *Appl. Phys.* 73: 379–381.

Shamsipur, M., A. Besharati-Seidani, J. Fasihi, and H. Sharghi. 2010. Synthesis and characterization of novel ion-imprinted polymeric nanoparticles for very fast and highly selective recognition of copper(II) ions. *Talanta* 83: 674–681.

Shan, J. and H. Tenhu. 2007. Recent advances in polymer protected gold nanoparticles: Synthesis, properties and applications (review). *Chem. Commun.* 44: 4580–4598.

Sharifkanov, A.Sh., Sh.S. Akhmedova, K.B. Murzagulova, and P.A. Galenko-Yaroshevskii. 2011. Richlokain—Dermatoprotecting pharmacological agent, Russian Patent No. 2261710.

Sheeney-Hai-Ichia, L., G. Sharabi, and I. Willner. 2002. Control of the electronic properties of thermosensitive poly(*N*-isopropylacrylamide) and Au-nano-particle/poly(*N*-isopropylacrylamide) composite hydrogels upon phase transition. *Adv. Funct. Mater*. 12: 27–32.

Shi, L., S. Khondee, T.H. Linz, and C. Berkland. 2008. Poly(*N*-vinylformamide) nanogels capable of pH-sensitive protein release. *Macromolecules* 41: 6546–6554.

Shiju, N.R. and V.V. Guliants. 2009. Recent developments in catalysis using nanostructured materials (review). *Appl. Catal. A: General* 356: 1–17.

Shikanov, A., A.J. Domb, and C.F. Weiniger. 2007. Long acting local anesthetic–polymer formulation to prolong the effect of analgesia. *J. Control. Release* 117: 97–103.

Shirsath, S.R., A.P. Hage, M. Zhou, S.H. Sonawane, and M. Ashokkumar. 2011. Bentonite nanoclay-FeCo nanocomposite hybrid hydrogel: A potential responsive sorbent for removal of organic pollutant from water. *Desalination* 281: 429–437.

Shirsath, S.R., A.P. Patil, R. Patil, J.B. Naik, P.R. Gogate, and Sh.H. Sonawane. 2013. Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: A comparative study. *Ultrason. Sonochem.* 20: 914–923.

Sigitov, V.B., S.E. Kudaibergenov, and E.A. Bekturov. 1987. Complexation of copper(II) with polyampholyte 2-methyl-5-vinylpyridine-acrylic acid in aqueous solution. *Koord. Khim.* 13: 600–604.

Singh, D.K. and S. Mishra. 2009. Synthesis, characterization and removal of Cd(II) using Cd(II)-ion imprinted polymer. *J. Hazard. Mater.* 164: 1547–1551.

Sivudu, K.S., N.M. Reddy, M.N. Prasad, K. Mohana Raju, Y. Murali Mohan, J.S. Yadav, G. Sabitha, and D. Shailaja. 2008. Highly efficient and reusable hydrogel-supported nano-palladium catalyst: Evaluation for Suzuki-Miyaura reaction in water. *J. Mol. Catal. A: Chem.* 295: 10–17.

Smirnov, D.I., T.V. Molchanova, L.I. Vodolazov, and V.A. Peganov. 2002. The sorption recovery of rare earth elements, yttrium and aluminum from the red mud. *Non-ferrous Metals* 8: 64–69.

Starodoubtsev, S.G., N.A. Churochkina, and A.R. Khokhlov. 2000. Hydrogel composites of neutral and slightly charged poly(acrylamide) gels with incorporated bentonite interaction with salt and ionic surfactants. *Langmuir* 16: 1529–1534.

Stein, D.B. 2009. *Handbook of Hydrogels: Properties, Preparation & Applications*. Nova Science Publishers, Inc., New York, 750pp.

Svetlichnyy, D.S., N.A. Dolya, Zh.E. Ibrayeva, and S.E. Kudaibergenov. 2009a. Immobilization of TiO_2 nanoparticles within poly(acrylamide) hydrogel matrix and evaluation of swelling behavior, thermodynamic parameters and mechanical properties of composite networks. *Materials of Russia-Kazakhstan-Japan Conference "Perspective technologies, equipment and analytical systems for material science and nanomaterials*," Volgograd, Russia, pp. 126–136.

Svetlichnyy, D.S., N.A. Dolya, Zh.E. Ibraeva, and S.E. Kudaibergenov. 2009b. Swelling behavior and mechanical properties of composite materials derived from poly(acrylamide) hydrogel and kaolin microparticles. *Bull. Kazakh Natl. Techn. Univ.* 4: 154–162.

Tanaka, Y., J.P. Gong, and Y. Osada. 2005. Novel hydrogels with excellent mechanical performance. *Prog. Polym. Sci.* 30: 1–9.

Taşdelen, B., N. Kayaman-Apohan, O. Güven, and B.M. Baysal. 2004. Preparation of poly(*N*-isopropylacrylamide/itaconic acid) copolymeric hydrogels and their drug release behavior. *Int. J. Pharm.* 78: 343–351.

Tatykhanova, G.S. 2009. Immobilization of biological active substances within the matrix of pH- and thermosensitive polymeric hydrogels. PhD thesis, A. Bekturov Institute of Chemical Sciences, Almaty, Kazakhstan, 109pp.

Tatykhanova, G., Zh. Sadakbayeva, D. Berillo, I. Galaev, Kh. Abdullin, Zh. Adilov, and S. Kudaibergenov. 2012. Metal complexes of amphoteric cryogels based on allylamine and methacrylic acid. *Macromol. Symp.* 317: 7–17.

Terlemezian, E., S. Veleva, and A. Arsov. 1990. Thermodynamic investigation of the sorption of Fe^{3+} and Cu^{2+} ions by a fibrous polyampholyte. *Acta Polym.* 40: 42–45.

Tokonami, S., H. Shiigi, and T. Nagaoka. 2009. Review: Micro- and nanosized molecularly imprinted polymers for high-throughput analytical applications. *Anal. Chim. Acta* 641: 7–13.

Uzu, O., R. Napier, and K. Ngwuobia. 2000. Gel technology applications in pipeline servicing. *Nigerian Annual International Conference and Exhibition*, Abuja, Nigeria, August 7–9, 2000.

Vasapollo, G., R. Del Sole, L. Mergola, M.R. Lazzoi, A. Scardino, S. Scorrano, and G. Mele. 2011. Molecularly imprinted polymers: Present and future prospective. *J. Mol. Sci*. 12: 5908–5945.

Verheyen, E., S. van der Wal, H. Deschout, K. Braeckmans, S. de Smedt, A. Barendregt, W.E. Hennink, and C.F. van Nostrum. 2011. Protein macromonomers containing reduction-sensitive linkers for covalent immobilization and glutathione triggered release from dextran hydrogels. *J. Control. Release* 156: 329–336.

Vesna, V.P., Z.P. Madzarevic, T. Volkov-Husovic, and S.J. Velickovic. 2013. Poly(methacrylic acid) based hydrogels as sorbents for removal of cationic dye basic yellow 28: Kinetics, equilibrium study and image analysis. *Chem. Eng. J.* 217: 192–204.

Wang, C., N.T. Flynn, and R. Langer. 2004a. Morphologically well-defined gold nanoparticles embedded in thermo-responsive hydrogel matrices. *Mater. Res. Soc. Symp. Proc.* 820: R2.2.1–R2.2.6.

Wang, C., N.T. Flynn, and R. Langer. 2004b. Controlled structure and properties of thermoresponsive nanoparticle–hydrogel composites. *Adv. Mater.* 16: 1074–1079.

Wang, G., K. Kuroda, T. Enoki, A. Grosberg, S. Masamune, T. Oya, Y. Takeoka, and T. Tanaka. 2000. Gel catalysts that switch on and off. *Proc. Natl. Acad. Sci. USA* 97: 9861–9864.

Wang, L., J. Zhang, and A. Wang. 2008. Removal of methylene blue from aqueous solution using chitosan-g-poly (acrylic acid)/montmorillonite superadsorbent nanocomposite. *Colloids Surf. A* 322: 47–53.

Wawrzkiewicz, M. 2013. Removal of C.I. Basic Blue 3 dye by sorption onto cation exchange resin, functionalized and non-functionalized polymeric sorbents from aqueous solutions and wastewaters. *Chem. Eng. J.* 217: 414–425.

Weissman, J.M., H.B. Sunkara, A.S. Tse, and S.A. Asher. 1996. Thermally switchable periodicities from novel mesocopically ordered materials. *Science* 274: 959–960.

Wen, W., W. Dongsheng, and L. Yuan. 2013. Controlled release of bovine serum albumin from stimuli-sensitive silk sericin based interpenetrating polymer network hydrogels. *Polym. Int.* 62: 1257–1262.

Whitcombe, M.J., M.E. Rodriguez, P. Villar, and E.N. Vulfson. 1995. A new method for the introduction of recognition site functionality into polymers prepared by molecular imprinting: Synthesis and characterization of polymeric receptors for cholesterol. *J. Am. Chem. Soc.* 117: 7105–7111.

Wizeman, W. and P. Kofinas. 2001. Molecularly imprinted polymer hydrogels displaying isomerically resolved glucose binding. *Biomaterials* 22: 1485–1491.

Wu, H., L. Wang, J. Zhang, Z. Shen, and J. Zhao. 2011. Catalytic oxidation of benzene, toluene and *p*-xylene over colloidal gold supported on zinc oxide catalyst. *Catal. Commun*. 12: 859–865.

Wu, W., W. Li, L.Q. Wang, K. Tu, and W. Sun. 2006. Synthesis and characterization of pH- and temperature-sensitive silk sericin/poly(*N*-isopropylacrylamide) interpenetrating polymer networks. *Polym. Int.* 55: 513–519.

Wulff, G. 1995. Molecular imprinting in cross-linked materials with the aid of molecular templates—A way towards artificial antibodies. *Angew. Chem. Int. Ed. Engl.* 34: 1812–1832.

Wunder, S., Y. Lu, M. Albrecht, and M. Ballauff. 2011. Catalytic activity of faceted gold nanoparticles studied by a model reaction: Evidence for substrate-induced surface restructuring. *ACS Catal*. 1: 908–916.

Xi, X., L. Yi, J. Shi, and S. Cao. 2003. Palladium complex of poly(4-vinylpyridine-*co*-acrylic acid) for homogeneous hydrogenation of aromatic nitro compounds. *J. Mol. Catal.: Chem.* 192: 1–7.

Xiang, Y., Zh. Peng, and D. Chen. 2006. A new polymer/clay nano-composite hydrogel with improved response rate and tensile mechanical properties. *Eur. Polym. J.* 42: 2125–2132.

Xie, F., G. Liu, F. Wu, G. Guo, and G. Li. 2012. Selective adsorption and separation of trace dissolved Fe(III) from natural water samples by double template imprinted sorbent with chelating diamines. *Chem. Eng. J.* 183: 372–380.

Xu, Sh., Sh. Zhang, and J. Yang. 2008. An amphoteric semi-IPN nanocomposite hydrogels based on intercalation of cationic polyacrylamide into bentonite. *Mater. Lett.* 62: 3999–4002.

Xu, S.M., S.F. Zhang, R.W. Lu, J.Z. Yang, and C.X. Cui. 2003. Study on adsorption behavior between Cr(VI) and crosslinked amphoteric starch. *J. Appl. Polym. Sci.* 89: 262–267.

Yang, X. and L. Ni. 2012. Synthesis of hybrid hydrogel of poly(AM-*co*-DADMAC)/silica sol and removal of methyl orange from aqueous solutions. *Chem. Eng. J*. 209: 194–200.

Yesmurzayeva, N., B. Selenova, and S. Kudaibergenov. 2013. Preparation and catalytic activity of gold nanoparticles stabilized by poly(*n*-vinylpyrrolidone) and deposited onto aluminum oxide. *Am. J. Nanomater.* 1: 1–4.

Yoshida, T., T.C. Lai, G.S. Kwon, and K. Sako. 2013. pH- and ion-sensitive polymers for drug delivery. *Expert Opin. Drug Deliv.* 10: 1497–1513.

Zhang, H., Y. Lu, G. Zhang, Sh. Gao, D. Sun, and Y. Zhong. 2008. Bupivacaine-loaded biodegradable poly(lactic-*co*-glycolic) acid microspheres: I. Optimization of the drug incorporation into the polymer matrix and modelling of drug release. *Int. J. Pharm.* 351: 244–249.

Zhang, J., B. Zhao, L. Meng, H. Wu, X. Wang, and Ch. Li. 2007. Controlled synthesis of gold nanospheres and single crystals in hydrogel. *J. Nanopart. Res.* 9: 1167–1171.

Zhang, Q., X. Li, Y. Zhao, and L. Chen. 2009. Preparation and performance of nanocomposite hydrogels based on different clay. *Appl. Clay Sci*. 46: 346–350.

Zhang, Y., R.W. Cattrall, I.D. McKelvie, and S.D. Kolev.2011. Gold, an alternative to platinum group metals in automobile catalytic converters (review). *Gold Bull*. 44(3): 145–153.

Zhang, Y.X., F.P. Wu, M.Zh. Li, and E.J. Wang. 2005. pH switching "on-off" semi-IPN hydrogel based on cross-linked poly(acrylamide-*co*-acrylic acid) and linear polyallylamine. *Polymer* 46: 7695–7700.

Zharmagambetova, A.K., N.A. Dolya, Zh.E. Ibrayeva, B.K. Dyussenalin, and S.E. Kudaibergenov. 2010. Physico-chemical and catalytic properties of polymer-protected and gel-immobilized palladium nanoparticles in hydrogenation of 2-propene-1-ol. *Bull. Acad. Sci. Repub. Kazakhstan, Ser. Chem*. 3: 6–9.

Zheksembayeva, N.A., G.S. Tatykhanova, D.K. Sabitova, V.B. Sigitov, and S.E. Kudaibergenov. 2012. Study of new composite hydrogel pigs for pipeline cleaning. *Intern. J. Transport&Logistic*. 12: 241–247.

Zhou, J., J. Ralston, R. Sedev, and D.A. Beattie. 2009. Functionalized gold nanoparticles: Synthesis, structure and colloid stability. *J. Colloid Interface Sci.* 331: 251–262.

Zhumaly, A.A., E.Yu. Blagikh, Zh.E. Ibrayeva, and S.E. Kudaibergenov. 2013. Preparation and properties of composite materials based on poly(acrylamide) hydrogel and clay minerals. *Bull. Kazakh Natl. Techn. Univ.* 5: 234–241.

References

1 Chapter 1: Composite Hydrogel Materials

Abdurrahmanoglu, S., V. Can, and O. Okay. 2008. Equilibrium swelling behavior and elastic properties of polymer-clay nanocomposite hydrogels. J. Appl. Polym. Sci. 109: 3714–3724.

Ahamed, M.E.H., X.Y. Mbianda, A.F. Mulaba-Bafubiandi, and L. Marjanovic. 2013. Selective extraction of gold(III) from metal chloride mixtures using ethylenediamine N-(2-(1imidazolyl)ethyl) chitosan ion-imprinted polymer. Hydrometallurgy 140: 1–13.

Ahmadi, S.J., O. Noori-Kalkhoran, and S. Shirvani-Arani. 2010. Synthesis and characterization of new ion-imprinted polymer for separation and preconcentration of uranyl (UO 2 2+) ions. J. Hazard. Mater. 175: 193–197.

Akdemir, S. and N. Kayaman-Apohan. 2007. Investigation of swelling, drug release and diffusion behaviors of poly(N-isopropylacrylamide)/poly(N-vinylpyrrolidone) full-IPN hydrogels. Polym. Adv. Technol. 18: 932–939.

Ali, Sh.A. and Sh.A. Haladu. 2013. A novel cross-linked poly zwitterion/anion having pHresponsive carboxylate and sulfonate groups for the removal of Sr 2+ from aqueous solution at low concentrations. React. Funct. Polym. 73: 796–804.

Ali, Sh.A. and O.Ch.S. Hamouz. 2012. Comparative solution properties of cyclocopolymers having cationic, anionic, zwitterionic and zwitterionic/anionic backbones of similar degree of polymerization. Polymer 53: 3368–3377.

Ali, Sh.A., O.Ch.S. Hamouz, and N.M. Hassan. 2013. Novel cross-linked polymers having pH-responsive amino acid residues for the removal of Cu 2+ from aqueous solution at low concentrations. J. Hazard. Mater. 248–249: 47–58.

Al-Yaari, M. 2011. Paraffin wax deposition: Mitigation and removal techniques. SPE Saudi Arabia Section Young Professionals Technical Symposium, Dhahran, Saudi Arabia, March 14–16, 2011.

An, F., B. Gao, X. Huang, Y. Zhang, Y. Li, Y. Xu, Z. Zhang, J. Gao, and Z. Chen. 2013. Selectively removal of Al(III) from Pr(III) and Nd(III) rare earth solution using surface imprinted polymer. React. Funct. Polym.73: 60–65.

Anderson, N.J., B.A. Bolto, R.J. Eldridge, and M.B. Jackson. 1993. Polyampholyts for water treatment with magnetic particles. React. Polym.19: 87–95.

Andersson, L.I. and K. Mobach. 1990. Enantiomeric resolution on molecularly imprinted polymers prepared with only non-covalent and non-ionic interactions. J. Chromatogr. 516(2): 313–322.

Anil, K.A. 2007. Stimuli-induced pulsatile or triggered release delivery systems for bioactive compounds. Recent patents on endocrine. Metab. Immun. Drug Discov. 1: 83–90.

Anish, K.G. and W.S. Abdul. 2012. Environmental responsive hydrogels: A novel approach in drug delivery system. J. Drug Deliv. Ther. 2: 81–88.

Annenkov, V.V., E.N. Danilovtzeva, V.V. Saraev, and I.A. Alsarsur. 2000. Interaction of copolymer of acrylic acid and 1-vinylimidazole with copper(ll) ions in aqueous solution. Izv. Russian Acad. Nauk Ser. Khim. 12: 2047–2054.

Annenkov, V.V., E.N. Danilovtseva, V.V. Saraev, and A.I. Mikhaleva. 2003. Complexation of copper(II) ions with imidazole–carboxylic polymeric systems. J. Polym. Sci. 41: 2256–2263.

Arasawa, H., C. Odawara, R. Yokoyama, H. Saitoh, T. Yamauchi, and N. Tsubokawa. 2004. Grafting of zwitterion-type polymers on to silica gel surface and their properties. React. Funct. Polym. 61: 153–161.

Arica, M.Y., H.A. Öktem, Z. Öktem, and S.A. Tuncel. 1999. Immobilization of catalase in poly(isopropylacrylamide-co-hydroxyethylmethacrylate) thermally reversible hydrogels. Polym. Int. 48: 879–884.

Avvaru, N.R., N.R. de Tacconi, and K. Rajeshwar. 1998. Compositional analysis of organicinorganic semiconductor composites. Analyst 123: 113–116.

Bajpai, A.K., S.K. Shukla, S. Bhanu, and S. Kankane. 2008. Responsive polymers in controlled drug delivery. Prog. Polym. Sci. 33: 1088–1118.

Balasubramanian, S.K., L. Yang, L.-Y.L. Yung, Ch.-N. Ong, W.-Y. Ong, and L.E. Yu. 2010. Characterization, purification, and stability of gold nanoparticles.

Biomaterials 31(34): 9023–9030.

Behbahani, M., A. Bagheri, M. Taghizadeh, M. Salarian, O. Sadeghi, L. Adlnasab, and K. Jalali. 2013. Synthesis and characterisation of nano structure lead (II) ion-imprinted polymer as a new sorbent for selective extraction and preconcentration of ultra trace amounts of lead ions from vegetables, rice, and ﬁsh samples. Food Chem. 138: 2050–2056.

Bekturganov, N.S., N.K. Tusupbayev, S.E. Kudaibergenov, G.S. Tatykhanova, L.V. Semushkina, and Zh.E. Ibrayeva. 2010. Method of recovery of rare earth elements from solution. Innovation Patent of Kazakhstan No. 24563.

Bekturov, E.A. and S.E. Kudaibergenov. 1996. Catalysis by Polymers. Huthig & Wepf Verlag, Heidelberg, Germany, 153pp.

Bekturov, E.A., S.E. Kudaibergenov, R.M. Iskakov, A.K. Zharmagambetova, Zh.E. Ibraeva, and S. Shmakov. 2010. Polymer-Protected Nanoparticles of Metals. Print-S Almaty, 274pp. (in Russian).

Bekturov, E.A., S.E. Kudaibergenov, and V.B. Sigitov. 1986. Complexation of amphoteric copolymer of 2-methyl-5-vinylpyridine-acrylic acid with copper(II) ions and catalase like activity of polyampholyte-metal complexes. Polymer 27: 1269–1272.

Bergbreiter, D.E., B.L. Case, Y.-S. Liu, and J.W. Caraway. 1998. Poly(N-isopropylacrylamide) soluble polymer supports in catalysis and synthesis. Macromolecules 31: 6053–6062.

Bergmann, N.M. and A.P. Nicholas. 2008. Molecular imprinted polymers with speciﬁc recognition for macromolecules and proteins. Prog. Polym. Sci. 33(3): 271–288.

Bessbousse, H., J.-F. Verchere, and L. Lebrun. 2012. Characterisation of metal-complexing membranes prepared by the semi-interpenetrating polymer networks technique. Application to the removal of heavy metal ions from aqueous solutions. Chem. Eng. J. 187: 16–28.

Birlik, E., A. Ersoz, E. Acıkkalp, A. Denizli, and R. Say. 2007. Cr(III)-imprinted polymeric beads: Sorption and preconcentration studies. J. Hazard. Mater. 140: 110–116.

Buengera, D., F. Topuza, and J. Groll. 2012. Hydrogels in sensing applications. Prog. Polym. Sci. 37: 1678–1719.

Byrne, M.E., K. Park, and N.A. Peppas. 2002. Molecular imprinting within hydrogels. Adv. Drug Deliv. Rev. 54: 149–161.

Byrne, M.E. and V. Salian. 2008. Molecular imprinting within hydrogels II: Progress and analysis of the field. Int. J. Pharm. 364: 188–212.

Cameron, A., H.S. Andersson, L.I. Andersson, R.J. Ansell, N. Kirsch, I.A. Nicholls, J. O’Mahony, and M.J. Whitcombe. 2006. Molecular imprinting science and technology: A survey of the literature for the years up to and including 2003. J. Mol. Recogn. 19: 106–180.

Cândido, J., A.G.B. Pereira, A.R. Fajardo, M.P.S. Ricardo Nágila, P.A. Feitosa Judith, C.M. Edvani, and H.A.R. Francisco. 2013. Poly(acrylamide-co-acrylate)/rice husk ash hydrogel composites II. Temperature effect on rice husk ash obtention. Compos. B Eng. 51: 246–253.

Casoloro, M., F. Bignotti, L. Sartore, and M. Penco. 2001. The thermodynamics of basic and amphoteric poly(amidoamine)s containing peptide nitrogens as potential binding sites for metal ions. Polymer 42: 903–912.

Chan, W.C. and J.Y. Wu. 2001. Dynamic adsorption behaviors between Cu^{2+} ion and waterinsoluble amphoteric starch in aqueous solutions. J. Appl. Polym. Sci. 81: 2849–2855.

Charles, O., S. Al Hamouz, and S.A. Ali. 2012. Removal of heavy metal ions using a novel cross-linked polyzwitterionic phosphonate. Sep. Purif. Technol. 98: 94–101.

Chauhan, G.S., B. Singh, and S. Kumar. 2005. Synthesis and characterization of N-vinyl pyrrolidone and cellulosics based functional graft copolymers for use as metal ions and ions and iodine sorbents. J. Appl. Polym. Sci. 98: 373–382.

Chauhan, K., G.S. Chauhan, and J.H. Ahn. 2009. Synthesis and characterization of novel guar gum hydrogels and their use as Cu^{2+} sorbents. J. Biotech. 100: 3599–3603.

Chen, H., D.M. Lentz, and R.C. Hedden. 2012a. Solution templating of Au and Ag nanoparticles by linear poly[2-(diethylamino)ethyl methacrylate]. J. Nanopart. Res. 14: 690–698.

Chen, H. and A. Wang. 2009. Adsorption characteristics of Cu(II) from aqueous solution onto poly(acrylamide)/attapulgite composite. J. Hazard. Mater. 165: 223–231.

Chen, S., H. Zhong, B. Gu, Y. Wang, X. Li, Zh. Cheng, L. Zhang, and Ch. Yao. 2012b. Thermosensitive phase behavior and drug release of in situ N-isopropylacrylamide copolymer. Mater. Sci. Eng. 32: 2199–2204.

Cheng, Y.-J., S. Zhou, and J.S. Gutmann. 2007. Morphology transition in ultrathin titania films: From pores to lamellae. Macromol. Rapid Commun. 28: 1392–1396.

Cho, E.Ch., J. Kim, A. Fernández-Nieves, and D.A. Weitz. 2008. Highly responsive hydrogel scaffolds formed by three-dimensional organization of microgel nanoparticles. Nanoletters 8: 168–172.

Chung, J.W., Y. Guo, S.-Y. Kwak, and R.D. Priestley. 2012. Understanding and controlling gold nanoparticle formation from a robust self-assembled cyclodextrin solid template. J. Mater. Chem. 22: 6017–6026.

Ciferri, A. and S.E. Kudaibergenov. 2007. Natural and synthetic polyampholytes. I. Theory and basic structures. Makromol. Rapid Commun. 28: 1953–1968.

Coughlan, D.C., F.P. Quilty, and O.I. Corrigan. 2004. Effect of drug physiochemical properties on swelling/deswelling kinetics and pulsatile drug release from thermoresponsive poly(N-isopropylacrylamide) hydrogels. J. Control. Release 98: 97–114.

Dai, J., P. Yao, N. Hua, P. Yang, and Y. Du. 2007. Preparation and characterization of polymerprotected Pt-Pt/Au core-shell nanoparticles. J. Dispersion Sci. Technol. 28: 872–875.

Dalaran, M., S. Emik, G. Güçlü, T.B. İyim, and S. Özgümüş. 2011. Study on a novel polyampholyte nanocomposite superabsorbent hydrogels: Synthesis, characterization and investigation of removal of indigo carmine from aqueous solution. Desalination 279: 170–182.

Dinu, M.V., M. Pradny, E.S. Dragan, and J. Michalek. 2013. Morphological and swelling properties of porous hydrogels based on poly(hydroxyethyl methacrylate) and chitosan modulated by ice-templating process and porogen leaching. J. Polym. Res. 20: 285.

Dolya, N., O. Rojas, S. Kosmella, B. Tiersch, J. Koetz, and S. Kudaibergenov. 2013. “One-pot” in situ formation of gold nanoparticles within poly(acrylamide) hydrogels. Macromol. Chem. Phys. 214: 114–121.

Dolya, N.A. 2009. Physico-chemical and catalytic properties of polymer-protected and gel-immobilized metals nanoparticles. PhD thesis, A. Bekturov Institute of Chemical Sciences, Almaty, Kazakhstan.

Dolya, N.A., Zh.E. Ibrayeva, E.A. Bekturov, and S.E. Kudaibergenov. 2009. Preparation, properties and catalytic activity of polymer-protected and gel-immobilized nanoparticles of gold, silver and palladium. Bull. Natl. Acad. Sci. Republic of Kazakhstan 4: 30–35.

Dolya, N.A., B.Kh. Musabayeva, M.G. Yashkrova, and S.E. Kudaibergenov. 2008a. Preparation, properties and catalytic activity of palladium nanoparticles immobilized within poly-N-isopropylacrylamide hydrogel matrix. Chem. J. Kazakhstan 1: 139–146.

Dolya, N.A., A.K. Zharmagambetova, B.Kh. Musabayeva, and S.E. Kudaibergenov. 2008b. Immobilization of polyethyleneimine-$[PdCl_4]^{-2}$ complexes into the matrix of polyacrylamide hydrogels and study of hydrogenation of allyl alcohol with the help of gelimmobilized nanocatalyst. Bull. Natl. Acad. Sci. Republic of Kazakhstan 1: 55–59.

Dorris, A., S. Rucareanu, L. Reven, C.J. Barrett, and R. Bruce Lennox. 2008. Preparation and characterization of polyelectrolyte-coated gold nanoparticles. Langmuir 24(6): 2532–2538.

Dragan, E.S. and D.F. Apopei Loghin. 2013. Enhanced sorption of Methylene Blue from aqueous solutions by semi-IPN composite cryogels with anionically modified potato starch entrapped in PAAm matrix. Chem. Eng. J. 234: 211–222.

Dragan, E.S. and M.V. Dinu. 2013. Design, synthesis and interaction with Cu^{2+} ions of ice templated composite hydrogels. Res. J. Chem. Environ. 17: 4–10.

Dunkin, I.R., J. Lenfeld, and D.C. Sherrington. 1993. Molecular imprinting of flat polycondensed aromatic-molecules in macroporous polymers. Polymer 34: 77–84.

Echeverria, C. and C. Mijangos. 2010. Effect of gold nanoparticles on the thermosensitivity, morphology, and optical properties of poly(acrylamide-acrylic acid) microgels. Macromol. Rapid Commun. 31: 54–58.

Eros, I., I. Csoka, E. Csanyi, and T.T. Wormsdorff. 2003. Examination of drug release from hydrogels. Polym. Adv. Technol. 14: 847–853.

Essawy, H. 2008. Poly(methyl methacrylate)-kaolinite nanocomposites prepared by interfacial polymerization with redox initiator system. Colloid Polym. Sci. 286: 795–803.

Fan, H.-T., J. Li, Z.-C. Li, and T. Sun. 2012. An ion-imprinted amino-functionalized silica gel sorbent prepared by hydrothermal assisted surface imprinting technique for selective removal of cadmium (II) from aqueous solution. Appl. Surf. Sci. 258: 3815–3822.

Feng, Q., F. Li, Q. Yan, Y.-C. Zhu, and C.-C. Ge. 2010. Frontal polymerization synthesis and drug delivery behavior of thermo-responsive poly(N-isopropylacrylamide) hydrogel. Colloid Polym. Sci. 288: 915–921.

Frimpong, R.A., S. Fraser, and J.Z. Hilt. 2006. Synthesis and temperature response analysis of magnetic-hydrogel nanocomposites. J. Biomed. Mater. Res. 80: 1–6.

Galaev, I.Y. and B. Mattiasson. 1999. ‘Smart’ polymers and what they could do in biotechnology and medicine. Trends Biotechnol. 17: 335–340.

Ge, F., M.-M. Li, H. Ye, and B.-X. Zhao. 2012. Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymer-modified magnetic nanoparticles. J. Hazard. Mater. 211–212: 366–372.

Godlewska-Żyłkiewicz, B., E. Zambrzycka, B. Leśniewska, and A.Z. Wilczewska. 2012. Separation of ruthenium from environmental samples on polymeric sorbent based on imprinted Ru(III)-allyl acetoacetate complex. Talanta 89: 352–359.

Gong, J.P., Y. Katsuyama, T. Kurokawa, and Y. Osada. 2003. Double-network hydrogels with extremely high mechanical strength. Adv. Mater. 15: 1155–1158.

Gorner, T., R. Gref, D. Michenot, F. Sommerb, M.N. Tranc, and E. Dellacherie. 1999. Lidocaine-loaded biodegradable nanospheres. Optimization of the drug incorporation into the polymer matrix. J. Control. Release 57: 259–268.

Hagiwara, H., Y. Shimizu, T. Hoshi, T. Suzuki, M. Ando, K. Ohkubo, and C. Yokoyama. 2001. Heterogeneous Heck reaction catalyzed by Pd/C in ionic liquid. Tetrahedron Lett. 42: 4349–4351.

Haraguchi, K., R. Farnworth, A. Ohbayashi, and T. Takehisa. 2003. Compositional effects on mechanical properties of nanocomposite hydrogels composed of poly(N,Ndimethylacrylamide) and clay. Macromolecules 36: 5732–5741.

Haraguchi, K. and H.J. Li. 2006. Mechanical properties and structure of polymer-clay nanocomposite gels with high clay content. Macromolecules 39: 1898–1905.

Haraguchi, K., K. Murata, and T. Takehisa. 2013. Stimuli-responsive properties of nanocomposite gels comprising (2-methoxyethylacrylate-co-N,N-dimethylacrylamide) copolymer-clay networks. Macromol. Symp. 329: 150–161.

Haraguchi, K. and T. Takehisa. 2002. Nanocomposite hydrogels: A unique organic–inorganic network structure with extraordinary mechanical, optical, and swelling/deswelling properties. Adv. Mater. 14: 1120–1124.

Haraguchi, K., T. Takehisa, and S. Fan. 2002. Effects of clay content on the properties of nanocomposite hydrogels composed of poly(N-isopropylacrylamide) and clay. Macromolecules 35: 10162–10171.

Haruta, M. 1997. Novel catalysis of gold deposited on metal oxides. Catal. Surveys Japan 1: 61–73.

Haruta, M. and M. Daté. 2001. Advances in the catalysis of Au nanoparticles (review). Appl. Catal. A: General 222: 427–437.

Hendrickson, O.D., A.V. Zherdev, and B.B. Dzantiyev. 2006. Molecularly imprinted polymers and their application in biochemical analysis. Achievements Biol. Chem. 46: 149–192.

Hoare, T.R. and D.S. Kohane 2008. Hydrogels in drug delivery: Progress and challenges. Polymer 49: 1993–2007.

Hoffman, A. and P.S. Stayton. 2004. Bioconjugates of smart polymers and proteins: Synthesis and application. Macromol. Symp. 207: 139–151.

Holgado, M.A., J.L. Arias, M.J. Cózar, J. Alvarez-Fuentes, A.M. Gañán-Calvo, and M. Fernández-Arévalo. 2008. Synthesis of lidocaine-loaded PLGA microparticles by flow focusing: Effects on drug loading and release properties. Int. J. Pharm. 358: 27–35.

Holtz, J.H. and S.A. Asher. 1997. Polymerized colloidal crystal hydrogel films as intelligent chemical sensing materials. Nature 389: 829–832.

Hoppe, C.E., M. Lazzari, I. Pardiñas-Blanco, and M.A. López-Quintela. 2006. One-step synthesis of gold and silver hydrosols using poly(N-vinyl-2-pyrrolidone) as a reducing agent. Langmuir 22: 7027–7034.

Ibrayeva, Zh.E. 2010. Composite polymer hydrogels. Chem. J. Kazakhstan 2: 165–175.

Ibrayeva, Zh.E., S.E. Kudaibergenov, and E.A. Bekturov. 2013. Stabilization of Metal Nanoparticles by Hydrophilic Polymers (in Russian). LAP Lambert Academic Publishing, Saarbrücken, Germany, 376pp.

Isobe, N., D. Lee, Y. Kwon, S. Kimura, Sh. Kuga, M. Wada, and U. Kim. 2011. Immobilization of protein on cellulose hydrogel. Cellulose 18: 1251–1256.

Jaggard, W.S. and A. Allen. 1977. Gel-like composition for use as a pig in a pipeline, US Patent No. 4003393.

Jagur-Grodzinski, J. 2010. Polymeric gels and hydrogels for biomedical and pharmaceutical applications. Polym. Adv. Technol. 21: 27–47.

James, D., G. Venkateswaran, and T. Prasada Rao. 2009. Removal of uranium from mining industry feed simulant solutions using trapped amidoxime functionality within a mesoporous imprinted polymer material. Microporous Mesoporous Mater. 119: 165–170.

Ji, X.Z., H.J. Liu, L.L. Wang, Y.K. Sun, and Y.W. Wu. 2013. Study on adsorption of Th(IV) using surface modified dibenzoylmethane molecular imprinted polymer. J. Radioanal. Nucl. Chem. 295: 265–270.

Jia, X., Y. Lia, B. Zhanga, Q. Chenga, and Sh. Zhanga. 2008. Preparation of poly(vinyl alcohol)/kaolinite nanocomposites via in situ polymerization. Mater. Res. Bull. 43: 611–617.

Jiajia G., C. Jibao, and S. Qingde. 2009. Ion imprinted polymer particles of neodymium: Synthesis, characterization and selective recognition. J. Rare Earths 27: 22.

Jiang, B. and Y. Zhang. 1993. Immobilization of catalase on crosslinked polymeric hydrogelseffect of anion on the activity of immobilized enzyme. Eur. Polym. J. 29: 1251–1254.

Jiang, H.Q., S. Manolache, A.C.L. Wong, and F.S. Denes. 2004. Plasma-enhanced deposition of silver nanoparticles onto polymer and metal surfaces for the generation of antimicrobial characteristics. J. Appl. Polym. Sci. 93: 1411–1422.

Jiang, W. and K. Irgum. 1999. Covalently bonded polymeric zwitterionic stationary phase for simultaneous separation of inorganic cations and anions. Anal. Chem. 71: 333–344.

Kabanov, V.A., A.A. Efendiev, and D.D. Orujev. 1977. Obtaining of complex-forming polymer sorbent with location of macromolecules “tuned” to the sorbed ion. Vysokomol. Soedin. Ser. B 19: 91–92.

Kabanov, V.A., A.A. Efendiev, and D.D. Orujev. 1979. Complex-forming polymeric sorbents with macromolecular arrangement favorable for ion sorption. J. Appl. Polym. Sci. 24: 259–267.

Kabiri, K. and M.J. Zohuriaan-Mehr. 2003. Superabsorbent hydrogel composites. Polym. Adv. Technol. 14: 438–444.

Kalfus, J., N. Singh, and A.J. Lesser. 2012. Reinforcement in nano-filled PAA hydrogels. Polymer 53: 2544–2547.

Kevadiya, B.D., G.V. Joshi, H.M. Mody, and H.C. Bajaj. 2011. Biopolymer–clay hydrogel composites as drug carrier: Host–guest intercalation and in vitro release study of lidocaine hydrochloride. Appl. Clay Sci. 52: 364–367.

Khvan, A.M., V.V. Chupov, O.V. Noa, and N.A. Plate. 1985. Experimental study of intramolecular crosslinking of poly-N-methacryloyl-l-lysine by copper(II) ions. Vysokomol. Soedin. Ser. A 27: 1243–1248.

Kidambi, S., J.H. Dai, J. Li, and M.L. Bruening. 2004. Selective hydrogenation by Pd nanoparticles embedded in polyelectrolyte multilayers. J. Am. Chem. Soc. 126:

2658–2659.

Kim, J.-H. and T.R. Lee. 2007. Hydrogel-templated growth of large gold nanoparticles: Synthesis of thermally responsive hydrogel-nanoparticle composites. Langmuir 23: 6504–6509.

Kirsch, N., C. Alexander, M. Lubke, M.J. Whitcombe, and E.N. Vulfson. 2000. Enhancement of selectivity of imprinted polymers via post-imprinting modification of recognition sites. Polymer 41: 5583–5590.

Klinger, D. and K. Landfester. 2012. Stimuli-responsive microgels for the loading and release of functional compounds: Fundamental concepts and applications. Polymer 53: 5209–5231.

Kohler, K., R.G. Heidenreich, J.G.E. Krauter, and M. Pietsch. 2001. Highly active palladium/ activated carbon catalysts for heck reactions: Correlation of activity, catalyst properties, and Pd leaching. Chem. Eur. J. 8: 622–631.

Kowalczyk, M., Z. Hubicki, and D. Kołodynska. 2013. Modern hybrid sorbents—New ways of heavy metal removal from waters. Chem. Eng. Proc. 70: 55–65.

Kudaibergenov, S.E. 2002. Polyampholytes: Synthesis, Characterization and Application. Kluwer Academic/Plenum Publishers, New York, 220pp.

Kudaibergenov, S.E. 2008. Polyampholytes. In: Encyclopedia of Polymer Material and Technology. John Wiley & Sons. Inc., pp. 1–30.

Kudaibergenov, S.E., Zh. Adilov, D. Berillo, G. Tatykhanova, Zh. Sadakbaeva, Kh. Abdullin, and I. Galaev. 2012b. Novel macroporous amphoteric gels: Preparation and characterization. Express Polym. Lett. 6: 346–353.

Kudaibergenov, S.E., L.A. Bimendina, and M.G. Yashkarova. 2007. Preparation and characterization of novel polymeric betaines based on aminocrotonates. J. Macromol. Sci. A: Pure Appl. Chem. 44: 899–912.

Kudaibergenov, S.E. and A. Ciferri. 2007. Natural and synthetic polyampholytes, functions and applications. Makromol. Rapid. Commun. 28: 1969–1986.

Kudaibergenov, S.E., N. Dolya, G. Tatykhanova, Zh.

Ibrayeva, B. Musabayeva, M. Yashkarova, and L. Bimendina. 2007. Semi-interpenetrating polymer networks of polyelectrolytes. Eurasian Chem. Technol. J. 9: 177–192.

Kudaibergenov, S.E., Zh.E. Ibraeva, N.A. Dolya, B.Kh. Musabayeva, A.K. Zharmagambetova, and J. Koetz. 2008. Semi-interpenetrating hydrogels of polyelectrolytes, polymer-metal complexes and polymer-protected palladium nanoparticles. Macromol. Symp. 274: 11–21.

Kudaibergenov, S.E., W. Jaeger, and A. Laschewsky. 2006. Polymeric betaines: Synthesis, characterization and application. Adv. Polym. Sci. 201: 157–224.

Kudaibergenov, S.E., N. Nueraje, and V. Khutoryanskiy. 2012a. Amphoteric nano-, micro-, and macrogels, membranes, and thin ﬁlms. Soft Matter 8: 9302–9321.

Kudaibergenov, S.E., G. Tatykhanova, and Zh. Ibraeva. 2011. Immobilization and controlled release of bioactive substances from stimuli-responsive hydrogels. Biodefence. NATO Science for Peace and Security Series-A: Chemistry and Biology. Springer, Dordrecht, The Netherlands, Chapter 19, pp. 79–188.

Kumar, A., A. Srivastava, I. Galaev, and B. Mattiasson. 2007. Smart polymers: Physical forms and bioengineering applications. Prog. Polym. Sci. 32: 1205–1237.

Kundakci, S., Ö.B. Üzüm, and E. Karadağ. 2008. Swelling and dye sorption studies of acrylamide/2-acrylamido-2-methyl-1-propanesulfonic acid/bentonite highly swollen composite hydrogels. React. Funct. Polym. 68: 458–473.

Kurokawa, Y. and M. Sasaki. 1982. Complexation between polyions and hydrous inorganic oxides and adsorption properties of complex. Makromol. Chem. 183: 679–685.

Lao, L.L. and R.V. Ramanujan. 2004. Magnetic and hydrogel composite materials for hyperthermia applications. J. Mater. Sci. Mater. Med. 15: 1061–1064.

Lázaro Martínez, J.M., M.F. Leal Denis, V. Campo Dall’Orto, and G.Y. Buldain. 2008a. Synthesis, FTIR, solid-state NMR and SEM studies of novel polyampholytes or polyelectrolytes obtained from EGDE, MAA and imidazoles. Eur. Polym. J. 44: 392–407.

Lázaro Martínez, J.M., M.F. Leal Denis, L.L. Piehl, E.

Rubín de Celis, G.Y. Buldain, and V.C. Dall'Orto. 2008b. Studies on the activation of hydrogen peroxide for color removal in the presence of a new Cu(II)-polyampholyte heterogeneous catalyst. Appl. Catal. Environ. 82: 273–283.

Lázaro Martínez, J.M., E. Rodríguez-Castellón, R.M. Torres Sánchez, L.R. Denaday, G.Y. Buldain, and V.C. Dall'Orto. 2011. XPS studies on the Cu(I,II)-polyampholyte heterogeneous catalyst: An insight into its structure and mechanism. J. Mol. Catal. 339: 43–51.

Leadbeater, N.E. and M. Marco. 2002. Ligand-free palladium catalysis of the Suzuki reaction in water using microwave heating. Org. Lett. 4(17): 2973–2976.

Lee, K.Y. and S.H. Yuk. 2007. Polymeric protein delivery systems. Prog. Polym. Sci. 32: 669–697.

Lee, W.F. and L.G. Yang. 2004. Superabsorbent polymeric materials. XII. Effect of montmorillonite on water absorbency for poly(sodium acrylate) and montmorillonite nanocomposite superabsorbents. J. Appl. Polym. Sci. 92: 3422–3429.

Lee, Y.-J. and P.V. Braun. 2003. Tunable inverse opal hydrogel pH sensors. Adv. Mater. 15: 563–566.

Li, Q., H. Liua, T. Liu, M. Guo, B. Qinga, X. Ye, and Z. Wu. 2010. Strontium and calcium ion adsorption by molecularly imprinted hybrid gel. Chem. Eng. J. 157: 401–407.

Li, S., Y. Wu, J. Wang, Q. Zhang, Y. Kou, and S. Zhang. 2010. Double-responsive polyampholyte as a nanoparticle stabilizer: Application to reversible dispersion of gold nanoparticles. J. Mater. Chem. 20: 4379–4384.

Li, Z.-C., H.-T. Fan, Yi. Zhang, M.-X. Chen, Z.-Y. Yu, X.-Q. Cao, and T. Sun. 2011. Cd(II)imprinted polymer sorbents prepared by combination of surface imprinting technique with hydrothermal assisted sol–gel process for selective removal of cadmium(II) from aqueous solution. Chem. Eng. J. 171: 703–710.

Lianga, R. and M. Liu. 2007. Preparation of poly(acrylic acid-co-acrylamide)/kaolin and release kinetics of urea from it. J. Appl. Polym. Sci. 106: 3007–3015.

Lianga, R., M. Liu, and L. Wu. 2007. Controlled release NPK compound fertilizer with the function of water retention.

React. Funct. Polym. 67: 769–779.

Lin, J., J. Wu, Z. Yang, and M. Pu. 2001. Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. Macromol. Rapid Commun. 22: 422–424.

Liu, D.Z., M.T. Sheu, C. Chen, Y.R. Yang, and H.O. Ho 2007. Release characteristics of lidocaine from local implant of polyanionic and polycationic hydrogels. J. Control. Release 118: 333–339.

Liusheng, Z., B. Brittany, and A. Frank. 2011. Stimuli responsive nanogels for drug delivery. Soft Matter 7: 5908–5916.

Lombardo Lupano, L.V., J.M. Lázaro Martínez, L.L. Piehl, E.R. de Celis, and V. Campo Dall'Orto. 2013. Activation of H 2 O 2 and superoxide production using a novel cobalt complex based on a polyampholyte. Appl. Catal. General 467: 342–354.

Lu, F., J. Ruiz, and D. Astruc. 2004. Palladium-dodecanethiolate nanoparticles as stable and recyclable catalysts for the Suzuki-Miyaura reaction of aryl halides under ambient conditions. Tetrahedron Lett. 45: 9443–9445.

Lu, Zh., G. Liu, and S. Duncan. 2003. Poly(2-hydroxyethyl acrylate-co-methyl acrylate)/SiO 2 / TiO 2 hybrid membranes. J. Membr. Sci. 221: 113–122.

Mahltig, B., N. Cheval, J.-F. Gohy, and A. Fahmi. 2010. Preparation of gold nanoparticles under presence of the diblock polyampholyte PMAA-b-PDMAEMA. J. Polym. Res. 17: 579–588.

Makysh, G.Sh., L.A. Bimendina, and S.E. Kudaibergenov. 2002. Interaction of richlocaine with some linear and crosslinked polymers. Polymer 43: 4349–4353.

Makysh, G.Sh., L.A. Bimendina, K.B. Murzagulova, and S.E. Kudaibergenov. 2003. Interaction of a new anesthetic drug richlocain with linear and weakly crosslinked polyn-vinylpyrrolidone. J. Appl. Polym. Sci. 89: 2977–2981.

Manpreet, K., Rajnibala, and A. Sandeep. 2013. Stimuli responsive polymers and their applications in drug delivery. Int. J. Adv. Pharm. Sci. 4: 477–495.

Marcin, K., J. Romanski, K. Michniewicz, J. Jurczak, and Z.

Stojek. 2010. Influence of polymer network-metal ion complexation on the swelling behaviour of new gels with incorporated α-amino acid groups. Soft Matter 6: 1336–1342.

Martínez, J.M.L., A.K. Chattah, G.A. Monti, M.F.L. Denis, G.Y. Buldain, and V. Campo Dall' Orto. 2008. New copper(II) complexes of polyampholyte and polyelectrolyte polymers: Solid-state NMR, FTIR, XRPD and thermal analyses. Polymer. 49: 5482–5489.

Martínez-Martínez, D., C. López-Cartes, A. Fernández, and J.C. Sánchez-López. 2008. Comparative performance of nanocomposite coatings of TiC or TiN dispersed in a-C matrixes. Surf. Coat. Technol. 203: 756–760.

Mattiasson, B., A. Kumar, and I. Yu Galaev. 2010. Macroporous Polymers: Applications, Production, Properties and Biotechnological/Biomedical Applications. CRC Press, Boca Raton, FL, 513pp.

Mayes, A.G. and M.J. Whitcombe. 2005. Synthetic strategies for the generation of molecularly imprinted organic polymers. Adv. Drug Deliv. Rev. 57: 1742–1778.

Metin, O., S. Sahin, and S. Ozkar. 2009. Water-soluble poly(4-styrenesulfonic acid-co-maleic acid) stabilized ruthenium(0) and palladium(0) nanoclusters as highly active catalysts in hydrogen generation from the hydrolysis of ammonia-borane. Int. J. Hydrogen Energy 34: 6304–6313.

Milasinovic, N., M.K. Krusic, Z. Knezevic-Jugovic, and J. Filipovic. 2010. Hydrogels of N-isopropylacrylamide copolymers with controlled release of a model protein. Int. J. Pharm. 383: 53–61.

Moore, B.M. 2000. Selective separation of rare earth elements by ion exchange in an iminodiacetic resin, US Patent No. 6093376.

Morrow, B.J., E. Matijević, and D.V. Goia. 2009. Preparation and stabilization of monodisperse colloidal gold by reduction with aminodextran. J. Colloid Interface Sci. 335: 62–69.

Mosbach, K. and O. Ramstrom. 1996. The emerging technique of molecular imprinting and its future impact on biotechnology. J. Biotechnol. 14: 163–170.

Motoyuki, I. and K. Hidehiro. 2009. Surface modification for improving the stability of nanoparticles in liquid media.

Kona Powder Part. J. 27: 119–129.

Nakamura, T. and M. Ogawa. 2013. Adsorption of cationic dyes within spherical particles of poly(N-isopropylacrylamide) hydrogel containing smectite. Appl. Clay Sci. 83–84: 469–473.

Nakayama, A., A. Kakugo, J.P. Gong, Y. Osada, M. Takai, T. Erata, and S. Kawano. 2004. High mechanical strength double-network hydrogel with bacterial cellulose. Adv. Funct. Mater. 14: 1124–1128.

Nicholls, I.A., O. Ramstrom, and K. Mosbach. 1995. Insights into the role of the hydrogenbond and hydrophobic effect on recognition in molecularly imprinted polymer synthetic peptide receptor mimics. J. Chromatogr. 691: 349–353.

Nishide, H., J. Deguchi, and E. Tsuchida. 1976. Selective adsorption of metal-ions on crosslinked poly(vinylpyridine) resin prepared with a metal-ion as a template. Chem. Lett. 5: 169–174.

Note, C., J. Koetz, L. Wattebled, and A. Laschewsky. 2007. Effect of a new hydrophobically modified polyampholyte on the formation of inverse microemulsions and the preparation of gold nanoparticles. J. Colloid Interface Sci. 308: 162–169.

Orozco-Guareño, E., F. Santiago-Gutiérrez, J.L. Morán-Quiroz, S.L. Hernandez-Olmos, V. Soto, W. de la Cruz, R. Manríquez, and S. Gomez-Salazar. 2010. Removal of Cu(II) ions from aqueous streams using poly(acrylic acid-co-acrylamide) hydrogels. J. Colloid Interface Sci. 349: 583–593.

Panic, V.V., Z.P. Madzarevic, T. Volkov-Husovic, and S.J. Velickovic. 2013. Poly(methacrylic acid) based hydrogels as sorbents for removal of cationic dye basic yellow 28: Kinetics, equilibrium study and image analysis. Chem. Eng. J. 217: 192–204.

Pardo-Yissar, V., R. Gabai, A.N. Shipway, T. Bourenko, and I. Willner. 2001. Gold nanoparticle/hydrogel composites with solvent-switchable electronic properties. Adv. Mater. 13: 1320–1323.

Park, T.G. 1993. Stabilization of enzyme immobilized in temperature-sensitive hydrogels. Biotechol. Lett. 15: 57–60.

Pavlyuchenko, V.N. and S.S. Ivanchev. 2009. Composite polymer hydrogels. Vysokomol. Soedin. Ser. A 51: 1075–1095.

Peppas, N.A., J.Z. Hilt, A. Khademhosseini, and R. Langer. 2006. Hydrogels in biology and medicine: From molecular principles to bionanotechnology. Adv. Mater. 18: 1345–1360.

Phan, N.T.S., D.H. Brown, and P. Styring. 2004. A polymer-supported salen-type palladium complex as a catalyst for the Suzuki-Miyaura cross-coupling reaction. Tetrahedron Lett. 45: 7915–7919.

Polakovič, M., T. Görner, R. Gref, and E. Dellacherie.1999. Lidocaine loaded biodegradable nanospheres: II. Modelling of drug release. J. Control. Release 60: 169–177.

Polyakov, M.V. 1931. Adsorption properties and structure of silica gel. Zh. Fiz. Khim. 2: 799–805.

Popa, M., N. Bajan, A.A. Popa, and A. Verestiuc. 2006. The preparation, characterization and properties of catalase immobilized on crosslinked gellan. J. Macromol. Sci. A: Pure Appl. Chem. 43: 355–367.

Qiu, Y. and K. Park. 2012. Environment-sensitive hydrogels for drug delivery. Adv. Drug Deliv. Rev. 64: 49–60.

Ram, S., L. Agrawal, A. Mishra, and S.K. Roy. 2011. Synthesis and optical properties of surface stabilized gold nanoparticles with poly(N-vinylpyrrolidone). Polymer molecules of a nanofluid. Adv. Sci. Lett. 4: 3431–3438.

Rammika, M., G. Darko, and N. Torto. 2011. Incorporation of Ni(II)-dimethylglyoxime ionimprinted polymer into electrospun polysulphone nanofibre for the determination of Ni(II) ions from aqueous samples. Water SA 37: 539–546.

Ray, S.S. and M. Okamoto. 2003. Polymer/layered silicate nanocomposite: A review from preparation to processing. Prog. Polym. Sci. 28: 1539–1641.

Rivas, B.L., S. Villegas, and B. Ruf. 2006. Water-insoluble polymers containing amine, sulfonic acid, and carboxylic acid groups: Synthesis, characterization, and metal-ionretention properties. J. Appl. Polym. Sci. 99: 3266–3274.

Romana, S., R.K. Ning, and N.Z. Richard. 2012. Surface-imprinted polymers in microfluidic devices. Sci.

China Chem. 55: 469–483.

Rutkevičius, M., S.K. Munusami, Z. Watson, A.D. Field, M. Salt, S.D. Stoyanov, J. Petkov, G.H. Mehl, and V.N. Paunov. 2012. Fabrication of novel lightweight composites by a hydrogel templating technique. Mater. Res. Bull. 47: 980–986.

Rychkov, V.N. 2003. Uranium sorption from sulfate solutions with polyampholytes. Radiochemistry (in Russian) 45: 56–60.

Rzaev, Z.M., S. Dinçer, and E. Pişkin. 2007. Functional copolymers of N-isopropylacrylamide for bioengineering applications. Prog. Polym. Sci. 32: 534–595.

Saber-Samandari, S. and M. Gazi. 2013. Cellulose-graft-polyacrylamide/hydroxyapatite composite hydrogel with possible application in removal of Cu (II) ions. React. Funct. Polym. 73: 1523–1530.

Sahiner, N. 2004. In situ metal particle preparation in cross-linked poly(2-acrylamido2-methyl-1-propansulfonic acid) hydrogel networks. Colloid Polym. Sci. 285: 283–292.

Sahiner, N. 2013. Soft and flexible hydrogel templates of different sizes and various functionalities for metal nanoparticle preparation and their use in catalysis. Prog. Polym. Sci. 38: 1329–1356.

Saraji, M. and H. Yousefi. 2009. Selective solid-phase extraction of Ni(II) by an ion-imprinted polymer from water samples. J. Hazard. Mater. 167: 1152–1157.

Sellergren, B. 1997. Noncovalent molecular imprinting: Antibody-like molecular recognition in polymeric network materials. Trends Anal. Chem. 16: 310–320.

Sellergren, B., B. Ekberg, and K. Mosbach. 1985. Molecular imprinting of amino acid derivatives in macroporous polymers. Demonstration of substrate and enantioselectivity by chromatographic resolution of racemic mixtures of amino acid derivatives. J. Chromatogr. A 347: 1–10.

Sershen, S.R., G.A. Mensing, M. Ng, N.J. Halas, D.J. Beebe, and J.L. West. 2005. Independent optical control of microfluidic valves formed from optomechanically responsive nanocomposite hydrogels. Adv. Mater. 17: 1366–1368.

Sershen, S.R., S.L. Westcott, N.J. Halas, and J.L. West.

2000. Temperature-sensitive polymer– nanoshell composites for photothermally modulated drug delivery. J. Biomed. Mater. Res. 51: 293–298.

Sershen, S.R., S.L. Westcott, J.L. West, and N.J. Halas. 2001. Anopto-mechanical nanoshellpolymer composite. Appl. Phys. 73: 379–381.

Shamsipur, M., A. Besharati-Seidani, J. Fasihi, and H. Sharghi. 2010. Synthesis and characterization of novel ion-imprinted polymeric nanoparticles for very fast and highly selective recognition of copper(II) ions. Talanta 83: 674–681.

Shan, J. and H. Tenhu. 2007. Recent advances in polymer protected gold nanoparticles: Synthesis, properties and applications (review). Chem. Commun. 44: 4580–4598.

Sharifkanov, A.Sh., Sh.S. Akhmedova, K.B. Murzagulova, and P.A. Galenko-Yaroshevskii. 2011. Richlokain—Dermatoprotecting pharmacological agent, Russian Patent No. 2261710.

Sheeney-Hai-Ichia, L., G. Sharabi, and I. Willner. 2002. Control of the electronic properties of thermosensitive poly(N-isopropylacrylamide) and Au-nano-particle/poly(Nisopropylacrylamide) composite hydrogels upon phase transition. Adv. Funct. Mater. 12: 27–32.

Shi, L., S. Khondee, T.H. Linz, and C. Berkland. 2008. Poly(N-vinylformamide) nanogels capable of pH-sensitive protein release. Macromolecules 41: 6546–6554.

Shiju, N.R. and V.V. Guliants. 2009. Recent developments in catalysis using nanostructured materials (review). Appl. Catal. A: General 356: 1–17.

Shikanov, A., A.J. Domb, and C.F. Weiniger. 2007. Long acting local anesthetic–polymer formulation to prolong the effect of analgesia. J. Control. Release 117: 97–103.

Shirsath, S.R., A.P. Hage, M. Zhou, S.H. Sonawane, and M. Ashokkumar. 2011. Bentonite nanoclay-FeCo nanocomposite hybrid hydrogel: A potential responsive sorbent for removal of organic pollutant from water. Desalination 281: 429–437.

Shirsath, S.R., A.P. Patil, R. Patil, J.B. Naik, P.R. Gogate, and Sh.H. Sonawane. 2013. Removal of Brilliant

Green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: A comparative study. Ultrason. Sonochem. 20: 914–923.

Sigitov, V.B., S.E. Kudaibergenov, and E.A. Bekturov. 1987. Complexation of copper(II) with polyampholyte 2-methyl-5-vinylpyridine-acrylic acid in aqueous solution. Koord. Khim. 13: 600–604.

Singh, D.K. and S. Mishra. 2009. Synthesis, characterization and removal of Cd(II) using Cd(II)-ion imprinted polymer. J. Hazard. Mater. 164: 1547–1551.

Sivudu, K.S., N.M. Reddy, M.N. Prasad, K. Mohana Raju, Y. Murali Mohan, J.S. Yadav, G. Sabitha, and D. Shailaja. 2008. Highly efficient and reusable hydrogel-supported nano-palladium catalyst: Evaluation for Suzuki-Miyaura reaction in water. J. Mol. Catal. A: Chem. 295: 10–17.

Smirnov, D.I., T.V. Molchanova, L.I. Vodolazov, and V.A. Peganov. 2002. The sorption recovery of rare earth elements, yttrium and aluminum from the red mud. Non-ferrous Metals 8: 64–69.

Starodoubtsev, S.G., N.A. Churochkina, and A.R. Khokhlov. 2000. Hydrogel composites of neutral and slightly charged poly(acrylamide) gels with incorporated bentonite interaction with salt and ionic surfactants. Langmuir 16: 1529–1534.

Stein, D.B. 2009. Handbook of Hydrogels: Properties, Preparation & Applications. Nova Science Publishers, Inc., New York, 750pp.

Svetlichnyy, D.S., N.A. Dolya, Zh.E. Ibrayeva, and S.E. Kudaibergenov. 2009a. Immobilization of TiO 2 nanoparticles within poly(acrylamide) hydrogel matrix and evaluation of swelling behavior, thermodynamic parameters and mechanical properties of composite networks. Materials of Russia-Kazakhstan-Japan Conference "Perspective technologies, equipment and analytical systems for material science and nanomaterials," Volgograd, Russia, pp. 126–136.

Svetlichnyy, D.S., N.A. Dolya, Zh.E. Ibraeva, and S.E. Kudaibergenov. 2009b. Swelling behavior and mechanical properties of composite materials derived from poly(acrylamide) hydrogel and kaolin microparticles. Bull. Kazakh Natl. Techn. Univ. 4: 154–162.

Tanaka, Y., J.P. Gong, and Y. Osada. 2005. Novel hydrogels with excellent mechanical performance. Prog. Polym. Sci. 30: 1–9.

Taşdelen, B., N. Kayaman-Apohan, O. Güven, and B.M. Baysal. 2004. Preparation of poly(Nisopropylacrylamide/itaconic acid) copolymeric hydrogels and their drug release behavior. Int. J. Pharm. 78: 343–351.

Tatykhanova, G.S. 2009. Immobilization of biological active substances within the matrix of pH- and thermosensitive polymeric hydrogels. PhD thesis, A. Bekturov Institute of Chemical Sciences, Almaty, Kazakhstan, 109pp.

Tatykhanova, G., Zh. Sadakbayeva, D. Berillo, I. Galaev, Kh. Abdullin, Zh. Adilov, and S. Kudaibergenov. 2012. Metal complexes of amphoteric cryogels based on allylamine and methacrylic acid. Macromol. Symp. 317: 7–17.

Terlemezian, E., S. Veleva, and A. Arsov. 1990. Thermodynamic investigation of the sorption of Fe^{3+} and Cu^{2+} ions by a fibrous polyampholyte. Acta Polym. 40: 42–45.

Tokonami, S., H. Shiigi, and T. Nagaoka. 2009. Review: Micro- and nanosized molecularly imprinted polymers for high-throughput analytical applications. Anal. Chim. Acta 641: 7–13.

Uzu, O., R. Napier, and K. Ngwuobia. 2000. Gel technology applications in pipeline servicing. Nigerian Annual International Conference and Exhibition, Abuja, Nigeria, August 7–9, 2000.

Vasapollo, G., R. Del Sole, L. Mergola, M.R. Lazzoi, A. Scardino, S. Scorrano, and G. Mele. 2011. Molecularly imprinted polymers: Present and future prospective. J. Mol. Sci. 12: 5908–5945.

Verheyen, E., S. van der Wal, H. Deschout, K. Braeckmans, S. de Smedt, A. Barendregt, W.E. Hennink, and C.F. van Nostrum. 2011. Protein macromonomers containing reduction-sensitive linkers for covalent immobilization and glutathione triggered release from dextran hydrogels. J. Control. Release 156: 329–336.

Vesna, V.P., Z.P. Madzarevic, T. Volkov-Husovic, and S.J. Velickovic. 2013. Poly(methacrylic acid) based hydrogels as sorbents for removal of cationic dye basic yellow 28:

Kinetics, equilibrium study and image analysis. Chem. Eng. J. 217: 192–204.

Wang, C., N.T. Flynn, and R. Langer. 2004a. Morphologically well-defined gold nanoparticles embedded in thermo-responsive hydrogel matrices. Mater. Res. Soc. Symp. Proc. 820: R2.2.1–R2.2.6.

Wang, C., N.T. Flynn, and R. Langer. 2004b. Controlled structure and properties of thermoresponsive nanoparticle–hydrogel composites. Adv. Mater. 16: 1074–1079.

Wang, G., K. Kuroda, T. Enoki, A. Grosberg, S. Masamune, T. Oya, Y. Takeoka, and T. Tanaka. 2000. Gel catalysts that switch on and off. Proc. Natl. Acad. Sci. USA 97: 9861–9864.

Wang, L., J. Zhang, and A. Wang. 2008. Removal of methylene blue from aqueous solution using chitosan-g-poly (acrylic acid)/montmorillonite superadsorbent nanocomposite. Colloids Surf. A 322: 47–53.

Wawrzkiewicz, M. 2013. Removal of C.I. Basic Blue 3 dye by sorption onto cation exchange resin, functionalized and non-functionalized polymeric sorbents from aqueous solutions and wastewaters. Chem. Eng. J. 217: 414–425.

Weissman, J.M., H.B. Sunkara, A.S. Tse, and S.A. Asher. 1996. Thermally switchable periodicities from novel mesocopically ordered materials. Science 274: 959–960.

Wen, W., W. Dongsheng, and L. Yuan. 2013. Controlled release of bovine serum albumin from stimuli-sensitive silk sericin based interpenetrating polymer network hydrogels. Polym. Int. 62: 1257–1262.

Whitcombe, M.J., M.E. Rodriguez, P. Villar, and E.N. Vulfson. 1995. A new method for the introduction of recognition site functionality into polymers prepared by molecular imprinting: Synthesis and characterization of polymeric receptors for cholesterol. J. Am. Chem. Soc. 117: 7105–7111.

Wizeman, W. and P. Kofinas. 2001. Molecularly imprinted polymer hydrogels displaying isomerically resolved glucose binding. Biomaterials 22: 1485–1491.

Wu, H., L. Wang, J. Zhang, Z. Shen, and J. Zhao. 2011. Catalytic oxidation of benzene, toluene and p-xylene over colloidal gold supported on zinc oxide catalyst. Catal. Commun. 12: 859–865.

Wu, W., W. Li, L.Q. Wang, K. Tu, and W. Sun. 2006. Synthesis and characterization of pH- and temperature-sensitive silk sericin/poly(N-isopropylacrylamide) interpenetrating polymer networks. Polym. Int. 55: 513–519.

Wulff, G. 1995. Molecular imprinting in cross-linked materials with the aid of molecular templates—A way towards arti�cial antibodies. Angew. Chem. Int. Ed. Engl. 34: 1812–1832.

Wunder, S., Y. Lu, M. Albrecht, and M. Ballauff. 2011. Catalytic activity of faceted gold nanoparticles studied by a model reaction: Evidence for substrate-induced surface restructuring. ACS Catal. 1: 908–916.

Xi, X., L. Yi, J. Shi, and S. Cao. 2003. Palladium complex of poly(4-vinylpyridine-co-acrylic acid) for homogeneous hydrogenation of aromatic nitro compounds. J. Mol. Catal.: Chem. 192: 1–7.

Xiang, Y., Zh. Peng, and D. Chen. 2006. A new polymer/clay nano-composite hydrogel with improved response rate and tensile mechanical properties. Eur. Polym. J. 42: 2125–2132.

Xie, F., G. Liu, F. Wu, G. Guo, and G. Li. 2012. Selective adsorption and separation of trace dissolved Fe(III) from natural water samples by double template imprinted sorbent with chelating diamines. Chem. Eng. J. 183: 372–380.

Xu, Sh., Sh. Zhang, and J. Yang. 2008. An amphoteric semi-IPN nanocomposite hydrogels based on intercalation of cationic polyacrylamide into bentonite. Mater. Lett. 62: 3999–4002.

Xu, S.M., S.F. Zhang, R.W. Lu, J.Z. Yang, and C.X. Cui. 2003. Study on adsorption behavior between Cr(VI) and crosslinked amphoteric starch. J. Appl. Polym. Sci. 89: 262–267.

Yang, X. and L. Ni. 2012. Synthesis of hybrid hydrogel of poly(AM-co-DADMAC)/silica sol and removal of methyl orange from aqueous solutions. Chem. Eng. J. 209: 194–200.

Yesmurzayeva, N., B. Selenova, and S. Kudaibergenov. 2013. Preparation and catalytic activity of gold nanoparticles stabilized by poly(n-vinylpyrrolidone) and deposited onto aluminum oxide. Am. J. Nanomater. 1: 1–4.

Yoshida, T., T.C. Lai, G.S. Kwon, and K. Sako. 2013. pH- and ion-sensitive polymers for drug delivery. Expert Opin. Drug Deliv. 10: 1497–1513.

Zhang, H., Y. Lu, G. Zhang, Sh. Gao, D. Sun, and Y. Zhong. 2008. Bupivacaine-loaded biodegradable poly(lactic-co-glycolic) acid microspheres: I. Optimization of the drug incorporation into the polymer matrix and modelling of drug release. Int. J. Pharm. 351: 244–249.

Zhang, J., B. Zhao, L. Meng, H. Wu, X. Wang, and Ch. Li. 2007. Controlled synthesis of gold nanospheres and single crystals in hydrogel. J. Nanopart. Res. 9: 1167–1171.

Zhang, Q., X. Li, Y. Zhao, and L. Chen. 2009. Preparation and performance of nanocomposite hydrogels based on different clay. Appl. Clay Sci. 46: 346–350.

Zhang, Y., R.W. Cattrall, I.D. McKelvie, and S.D. Kolev.2011. Gold, an alternative to platinum group metals in automobile catalytic converters (review). Gold Bull. 44(3): 145–153.

Zhang, Y.X., F.P. Wu, M.Zh. Li, and E.J. Wang. 2005. pH switching “on-off” semi-IPN hydrogel based on cross-linked poly(acrylamide-co-acrylic acid) and linear polyallylamine. Polymer 46: 7695–7700.

Zharmagambetova, A.K., N.A. Dolya, Zh.E. Ibrayeva, B.K. Dyussenalin, and S.E. Kudaibergenov. 2010. Physico-chemical and catalytic properties of polymer-protected and gel-immobilized palladium nanoparticles in hydrogenation of 2-propene-1-ol. Bull. Acad. Sci. Repub. Kazakhstan, Ser. Chem. 3: 6–9.

Zheksembayeva, N.A., G.S. Tatykhanova, D.K. Sabitova, V.B. Sigitov, and S.E. Kudaibergenov. 2012. Study of new composite hydrogel pigs for pipeline cleaning. Intern. J. Transport&Logistic. 12: 241–247.

Zhou, J., J. Ralston, R. Sedev, and D.A. Beattie. 2009. Functionalized gold nanoparticles: Synthesis, structure and colloid stability. J. Colloid Interface Sci. 331: 251–262.

Zhumaly, A.A., E.Yu. Blagikh, Zh.E. Ibrayeva, and S.E. Kudaibergenov. 2013. Preparation and properties of

composite materials based on poly(acrylamide) hydrogel and
clay minerals. Bull. Kazakh Natl. Techn. Univ. 5: 234-241.

2 Chapter 2: Cryogels for Affinity Chromatography

Ahmed, N., G. Barker, K. Oliva, D. Garfin, G. Rice. 2003. An approach to remove albumin for the proteomic analysis of low abundance biomarkers in human serum. Proteomics 3: 1980–1987.

Akduman, B., M. Uygun, D.A. Uygun, S. Akgöl, A. Denizli. 2013. Purification of yeast alcohol dehydrogenase by using immobilized metal affinity cryogels. Mater. Sci. Eng. C 33: 4842–4848.

Alexander, C., H. Andersson, L. Andersson, R. Ansell, N. Kirsch, I.A. Nicholls, J. Mahony, M.J. Whitcombe. 2006. Molecular imprinting science and technology: A survey of the literature for the years up to and including 2003. J. Mol. Recognit. 19: 106–180.

Alkan, H., N. Bereli, Z. Baysal, A. Denizli. 2009. Antibody purification with protein A attached supermacroporous PHEMA cryogel. Biochem. Eng. J. 45: 201–208.

Altıntaş, E.B., A. Denizli. 2009. Monosize magnetic hydrophobic beads for lysozyme purification under magnetic field. Mater. Sci. Eng. C 29: 1627–1634.

Altıntaş, E.B., N. Tüzmen, L. Uzun, A. Denizli. 2007. Immobilized metal affinity adsorption for antibody depletion from human serum with monosize beads. Ind. Eng. Chem. Res. 46: 7802–7810.

Andaç, M., G. Baydemir, H. Yavuz, A. Denizli. 2012. Molecularly imprinted composite cryogel for albumin depletion from human serum. J. Mol. Recognit. 25: 555–563.

Andaç, M., I.Y. Galaev, A. Denizli. 2013. Molecularly imprinted poly(hydroxyethyl methacrylate) based cryogel for albumin depletion from human serum. Colloids Surf. B 109: 259–265.

Andaç, M., F.M. Plieva, A. Denizli, I.Y. Galaev, B. Mattiasson. 2008. Poly(hydroxyethyl methacrylate)-based macroporous hydrogels with disulfide cross-linker. Macromol. Chem. Phys. 209: 577–584.

Andersson, N.L., N.G. Anderson. 2002. The human plasma proteome. Mol. Cell. Proteomics 11: 845–867.

Arvidsson, P., F.M. Plieva, V.I. Lozinsky, I.Y. Galaev, B.

Mattiasson. 2003. Direct chromatographic capture of enzyme from crude homogenate using immobilized metal affinity chromatography on a continuous supermacroporous adsorbent. J. Chromatogr. A 986: 275–290.

Arvidsson, P., F.M. Plieva, I.N. Savina, V.I. Lozinsky, S. Fexby, L. Bülow, I. Yu. Galaev, B. Mattiasson. 2002. Chromatography of microbial cells using a continuous supermacroporous affinity and ion-exchange column. J. Chromatogr. A 977: 27–38.

Aslıyüce, S., L. Uzun, A.Y. Rad, S. Ünal, R. Say, A. Denizli. 2012. Molecular imprinting based composite cryogel membranes for purification of anti-hepatitis B surface antibody by fast protein liquid chromatography. J. Chromatogr. B 889–890: 95–102.

Aslıyüce, S., L. Uzun, R. Say, A. Denizli. 2013. Immunoglobulin G recognition with Fab fragments imprinted monolithic cryogels: Evaluation of the effects of metal-ion assistedcoordination of template molecule. React. Funct. Polym. 73: 813–820.

Avcibaşi, N., M. Uygun, M.E. Çorman, S. Akgöl, A. Denizli. 2010. Application of supermacroporous monolithic hydrophobic cryogel in capturing of albumin. Appl. Biochem. Biotechnol. 162: 2232–2243.

Babaç, C., H. Yavuz, I.Y. Galaev, E. Pişkin, A. Denizli. 2006. Binding of antibodies to concanavalin A modified monolithic cryogel. React. Funct. Polym. 66: 1263–1271.

Bakhspour, M., N. Bereli, S. Şenel. 2014. Preparation and characterization of thiophilic cryogels with 2-mercaptoethanol as the ligand for IgG purification. Colloids Surf. B 113: 261–268.

Bereli, N., M. Andac, G. Baydemir, R. Say, I.Y. Galaev, A. Denizli. 2008. Protein recognition via ion coordinated molecularly imprinted supermacroporous cryogels. J. Chromatogr. A 1190: 18–26.

Bereli, N., G. Ertürk, A. Denizli. 2012. Histidine containing macroporous affinity cryogels for immunoglobulin G purification. Sep. Sci. Technol. 47: 1813–1820.

Bereli, N., G. Şener, E.B. Altintaş, H. Yavuz, A. Denizli. 2010. Poly(glycidyl methacrylate) beads embedded cryogels for pseudo-specific affinity depletion of albumin and immunoglobulin G. Mater. Sci. Eng. 30: 323–329.

Bhattacharyya, R., R.P. Saha, U. Samana, P. Chakrabarti. 2003. Geometry of interaction of the histidine ring with other planar and basic residues. J. Proteome Res. 2: 255–263.

Bibi, N.S., N.K. Singh, R.N. Dsouza, M. Aasim, M. Fernandez-Lahore. 2013. Synthesis and performance of megaporous immobilized metal-ion affinity cryogels for recombinant protein capture and purification. J. Chromatogr. A 1272: 145–149.

Cao, X., R. Eisenthal, J. Hubble. 2002. Detachment strategies for affinity adsorbed-cells. Enzyme Microb. Technol. 31: 153–160.

Carman, W.F. 1997. The clinical significance of surface antigen variants of hepatitis B virus. J. Viral Hepat. 4: 11–20.

Carter, P.J. 2006. Potent antibody therapeutics by design. Nat. Rev. Immunol. 6: 343–357.

Çimen, D., A. Denizli. 2012. Immobilized metal affinity monolithic cryogels for cytochrome c purification. Colloids Surf. B 93: 29–35.

Cuatrecasas, P., M. Wilchek, C.B. Anfinsen. 1968. Selective enzyme purification by affinity chromatography. Proc. Natl. Acad. Sci. USA 61: 636–643.

Dainiak, M.B., A. Kumar, I.Y. Galaev, B. Mattiasson. 2006. Detachment of affinity-captured bioparticles by deformation of a macroporous hydrogel. Proc. Natl. Acad. Sci. USA 103: 849–854.

Dainiak, M.B., F.M. Plieva, I.Y. Galaev, R. Hatti-Kaul, B. Mattiasson. 2005. Cell chromatography: Separation of different microbial cells using IMAC supermacroporous monolithic columns. Biotechnol. Prog. 21: 644–649.

Das, S., S. Banerjee, J. Dasgupta. 1992. Experimental evaluation of preventive and therapeutic potentials of lysozyme. Chemotherapy 38: 350–357.

Demiryas, N., N. Tuzmen, I.Y. Galaev, E. Piskin, A. Denizli. 2007. Poly(acrylamide-allyl glycidyl ether) cryogel as a stationary phase in dye affinity chromatography. J. Appl. Polym. Sci. 105: 1808–1816.

Denizli, A. 2011. Purification of antibodies by affinity chromatography. Hacettepe J. Biol. Chem. 39: 1–18.

Denizli, A., E. Pişkin. 2001. Dye-ligand affinity systems. J. Biochem. Biophys. Methods 49: 391–416.

Derazshamshir, A., G. Baydemir, M. Andaç, R. Say, I.Y. Galaev, A. Denizli. 2010. Molecularly imprinted PHEMA-based cryogel for depletion of hemoglobin from human blood. Macromol. Chem. Phys. 211: 657–668.

Dragan, E.S, M.V. Dinu. 2013. Design, synthesis and interaction with Cu 2+ ions of ice templated composite hydrogels. Res. J. Chem. Environ. 17: 4–10.

Emir, S., R. Say, H. Yavuz, A. Denizli. 2004. A new metal chelate affinity adsorbent for cytochrome c. Biotechnol. Prog. 20: 223–228.

Engler, A.J., L. Richert, J.Y. Wong, C. Picart, D.E. Discher. 2004. Surface probe measurements of the elasticity of sectioned tissue, thin gels and polyelectrolyte multilayer films: Correlations between substrate stiffness and cell adhesion. Surf. Sci. 570: 142–154.

Füglistaller, P. 1989. Comparison of immunoglobulin binding capacities and ligand leakage using eight different protein A affinity matrices. J. Immunol. Methods 124: 171–177.

Gagnon, P. 2012. Technology trends in antibody purification. J. Chromatogr. A 1221: 57–70.

Gagnon, P. 2013. Emerging challenges to protein A: Chromatin-directed clarification enables new purification options. Bioprocess Int. 11: 44–52.

Galaev, I.Y., M.B. Dainiak, F.M. Plieva, R. Hatti-Kaul, B. Mattiasson. 2005. High throughput processing of particulate-containing samples using supermacroporous elastic monoliths in microtiter (multiwall) plate format. J. Chromatogr. A 1065: 169–175.

Ghosh, R., S.S. Silva, Z.F. Cui. 2000. Lysozyme separation by hollow fibre ultrafiltration. Biochem. Eng. J. 6: 19–24.

Gomez-Suarez, C., H.J. Busscher, H.C. van der Mei. 2001. Analysis of bacterial detachment from substrate surfaces by the passage of air-liquid interface. Appl. Environ. Microbiol. 67: 2531–2537.

Hajizadeh, S., H. Kirsebom, A. Leistner, B. Mattiasson. 2012. Composite cryogel with immobilized concanavalin A for affinity chromatography of glycoproteins. J. Sep. Sci. 35: 2978–2985.

Hajizadeh, S., C. Xu, H. Kirsebom, L. Ye, B. Mattiasson. 2013. Cryogelation of molecularly imprinted nanoparticles: A macroporous structure as affinity chromatography column for removal of b-blockers from complex samples. J. Chromatogr. A 1274: 6–12.

Hari, P.R., W. Paul, C.P. Sharma. 2000. Adsorption of human IgG on Cu(II)-immobilized cellulose affinity membrane: Preliminary study. J. Biomed. Mater. Res. 50: 110–113.

Heftman, E., ed. 2004. Chromatography: Fundamentals and Applications of Chromatography and Related Differential Migration Methods, Part B, 6th edn. Elsevier, Amsterdam, the Netherlands.

Hsu, H.Y., M.H. Chang, S.H. Liaw, Y.H. Ni, H.L. Chen. 1999. Changes of hepatitis B surface antigen variants in carrier children before and after universal vaccination. Hepatology 30: 1312–1317.

Hutchens, T.W., J. Porath. 1986. Thiophilic adsorption of immunoglobulins-analysis of conditions optimal for selective immobilization and purification. Anal. Biochem. 159: 217–226.

Kumar, A., F.M. Plieva, I.Y. Galaev, B. Mattiasson. 2003. Affinity fractionation of lymphocytes using a monolithic cryogel. J. Immunol. Methods 283: 185–194.

Labib, M., M. Hedström, M. Amin, B. Mattiasson. 2009. A multipurpose capacitive biosensor for assay and quality control of human IgG. Biotechnol. Bioeng. 104: 312–320.

Langone, J.J. 1982. Applications of immobilized protein A in immunochemical techniques. J. Immunol. Methods 55: 277–296.

Le Noir, M., F. Plieva, T. Hey, B. Guieyse, B. Mattiasson. 2007. Macroporous molecularly imprinted polymer/cryogel composite systems for the removal of endocrine disrupting trace contaminants. J. Chromatogr. A 1154: 158–164.

Low, D., R. O'Leary, N.S. Pujar. 2007. Future of antibody purification. J. Chromatogr. B 848: 48–63.

Lozinsky, V.I., F.M. Plieva, I.Y. Galaev, B. Mattiasson. 2001. The potential of polymeric cryogels in bioseparation. Bioseparation 10: 163–188.

Madigan, M.T., J.M. Martinko, J. Parker. 2000. Brock Biology of Microorganisms. Prentice- Hall, Upper Saddle River, NJ.

Mammen, M., S.K. Choi, G.M. Whitesides. 1998. Polyvalent interactions in biological systems: Implications for design and use of multivalent ligands and inhibitors. Angew. Chem. Int. Ed. 37: 2754–2794.

Matejtschuk, P., ed. 1997. Affinity Separations: A Practical Approach. IRL Press, Oxford, U.K.

McCoy, M., K. Kalghatgi, F.E. Regnier, N. Afeyan. 1996. Perfusion chromatography— Characterization of column packings for chromatography. J. Chromatogr. A 743: 221–229.

Ming, F., W.J.D. Whish, J. Hubble. 1998. Estimation of parameters for cell-surface interactionsmaximum binding force and detachment constant. Enzyme Microb. Technol. 22: 94–99.

Noppe, W., F.M. Plieva, K. Vanhoorelbeke, H. Deckmyn, M. Tuncel, A. Tuncel, I.Y. Galaev, B. Mattiasson. 2007. Macroporous monolithic gels, cryogels, with immobilized phages from phage-display library as a new platform for fast development of af�nity adsorbent capable of target capture from crude feeds. J. Biotechnol. 131: 293–299.

Odabaşı, M., G. Baydemir, M. Karataş, A. Derazshamshir. 2011. Preparation and characterization of metal-chelated poly(HEMA-MAH) monolithic cryogels and their use for DNA adsorption. J. Appl. Polym. Sci. 116: 1306–1312.

Pelta, J., H. Berry, G.C. Fadda, E. Pauthe, D. Lairez. 2000. Statistical conformation of human plasma �bronectin. Biochemistry 39: 5146–5154.

Perçin, I., E. Aksoz, A. Denizli. 2013. Gelatin-immobilised poly(hydroxyethyl methacrylate) cryogel for af�nity puri�cation of �bronectin. Appl. Biochem. Biotechnol. 171: 352–365.

Perçin, I., E. Sağlar, H. Yavuz, E. Aksöz, A. Denizli. 2011. Poly(hydroxyethyl methacrylate) based af�nity cryogel for plasmid DNA puri�cation. Int. J. Biol. Macromol. 48:

577–582.

Perçin, I., H. Yavuz, E. Aksöz, A. Denizli. 2012. Mannose-speci c lectin isolation from Canavalia ensiformis seeds by PHEMA-based cryogel. Biotechnol. Prog. 28: 756–761.

Reichert, J.M., C.J. Rosesweig, L.B. Faden, M.C. Dewitz. 2005. Monoclonal antibody successes in the clinic. Nat. Biotechnol. 23: 1073–1078.

Rosa, P.A.J., I.F. Ferreira, A.M. Azevedo, M.R. Aires-Barros. 2010. Aqueous two-phase systems: A viable-platform in the manufacturing of biopharmaceuticals. J. Chromatogr. A 1217: 2296–2305.

Sato, A.K., D.J. Sexton, L.A. Morganelli, E.H. Cohen, Q.L. Wu, G.P. Conley, Z. Streltsova et al. 2002. Development of mammalian serum albumin puri cation media by peptide phage display. Biotechnol. Prog. 18: 182–192.

Shibayama, M., T. Tanaka. 1993. Volume phase transition and related phenomena of polymer gels. In Responsive Gels: Volume Transitions I, Dusek, K. (ed.). Springer, Berlin, Germany, pp. 1–62.

Shukla, A.A., J. Thömmes. 2010. Recent advances in large-scale production of monoclonal antibodies and related proteins. Trends Biotechnol. 28: 253–261.

Sousa, C., A. Cebolla, V. DeLorenzo. 1996. Enhanced metalloadsorption of bacterial cells displaying poly-His peptides. Nat. Biotechnol. 14: 1017–1020.

Sun, S., Y. Tang, Q. Fu, X. Liu, M. Guo, Y. Zhao, C. Chang. 2012a. Monolithic cryogels made of agarose-chitosan composite and loaded with agarose beads for puri cation of immunoglobulin G. Int. J. Biol. Macromol. 50: 1002–1007.

Sun, S., Y. Yang, Q. Fu, X. Liu, W. Du, K. Guo, Y. Zhao. 2012b. Preparation of agarose/ chitosan composite cryogels for af nity puri cation of glycoproteins. J. Sep. Sci. 35: 893–900.

Takeuchi, T., T. Hishiya. 2008. Molecular imprinting of proteins emerging as a tool for protein recognition. Org. Biomol. Chem. 6: 2459–2467.

Tamahkar, E., N. Bereli, R. Say, A. Denizli. 2011. Molecularly imprinted supermacroporous cryogels for cytochrome c recognition. J. Sep. Sci. 34: 3433–3440.

Tekiner, P., I. Perçin, B. Ergün, H. Yavuz, E. Aksöz. 2012. Purification of urease from jack bean with copper(II) chelated PHEMAH cryogels. J. Mol. Recognit. 25: 549–554.

Tirumalai, R.S., K.C. Chan, D.A. Prieto, H.J. Issaq, T.P. Conrads, T.D. Veenstra. 2003. Characterization of the low molecular weight human serum proteome. Mol. Cell. Proteomics 2: 1096–1103.

Urthaler, J., R. Schlegl, A. Podgornik, A. Strancar, A. Jungbauer, R. Necina. 2005. Application of monoliths for plasmid DNA purification, development and transfer to production. J. Chromatogr. A 1065: 93–106.

Uygun, D.A., B. Akduman, M. Uygun, S. Akgöl, A. Denizli. 2012. Purification of papain using Reactive Green 5 attached supermacroporous monolithic cryogel. Appl. Biochem. Biotechnol. 167: 552–563.

Uygun, D.A., M.E. Çorman, N. Öztürk, S. Akgöl, A. Denizli. 2010. Poly(hydroxyethyl methacrylate-methacryloyl amino tryptophan) nanospheres and their utilization as affinity adsorbents for lipase adsorption. Mater. Sci. Eng. C 30: 1285–1290.

Üzek, R., L. Uzun, S. Şenel, A. Denizli. 2013. Nanospines incorporation into the structure of the hydrophobic cryogels via novel cryogelation method: An alternative sorbent for plasmid DNA purification. Colloids Surf. B 102: 243–250.

Vijayalakshmi, M.A. 1989. Pseudobiospecific ligand affinity chromatography. Trends Biotechnol. 7: 71–76.

Vijayalakshmi, M.A. 1996. Histidine ligand affinity chromatography. Mol. Biotechnol. 6: 347–357.

Wang, C., X.Y. Dong, Z. Jiang, Y. Sun. 2013. Enhanced adsorption capacity of cryogel bed by incorporating polymeric resin particles. J. Chromatogr. A 1272: 20–25.

Wang, Y.Y., P. Cheng, D.W. Chan. 2003. A simple affinity spin tube filter method for removing high-abundant common proteins on enriching low-abundant biomarkers for serum proteomic analysis. Proteomics 3: 243–248.

Wilchek, M. 2004. My life with affinity. Protein Sci. 13: 3066–3070.

Wong, J.Y., J.B. Leach, X.Q. Brown. 2004. Balance of chemistry, topography, and mechanics at the cell-biomaterial interface: Issues and challenges for assessing the role of substrate mechanics on cell response. Surf. Sci. 570: 119–133.

Yao, K., S. Shen, J. Yun, L. Wang, F. Chen, X. Yu. 2007. Protein adsorption in supermacroporous cryogels with embedded nanoparticles. Biochem. Eng. J. 36: 139–146.

Yao, K., J. Yun, S. Shen, L. Wang, X. He, X. Yu. 2006. Characterization of a novel continuous supermacroporous monolithic cryogel embedded with nanoparticles for protein chromatography. J. Chromatogr. A 1109: 103–110.

Yilmaz, F., N. Bereli, H. Yavuz, A. Denizli. 2009. Supermacroporous hydrophobic affinity cryogels for protein chromatography. Biochem. Eng. J. 43: 272–279.

Yun, J., J.T. Dafoe, E. Peterson, L. Xu, S.J. Yao, A.J. Daugulis. 2013. Rapid freezing cryopolymerization and microchannel liquid-flow focusing for cryogel beads: Adsorbent preparation and characterization of supermacroporous bead-packed bed. J. Chromatogr. A 1284: 148–154.

3 Chapter 3: Particulate/Cell Separations Using Macroporous Monolithic Matrices

Ahlqvist, J., A. Kumar, H. Sundstrom, E. Ledung, E.G. Hornsten, S.O. Enfors, and B. Mattiasson. 2006. Affinity binding of inclusion bodies on supermacroporous monolithic cryogels using labeling with specific antibodies. J. Biotechnol. 122: 216–225.

Annaka, M., T. Matsuura, M. Kasai, T. Nakahira, Y. Hara, and T. Okano. 2003. Preparation of comb-type N-isopropylacrylamide hydrogel beads and their application for sizeselective separation media. Biomacromolecules 4: 395–403.

Aprilita, N.H., C.W. Huck, R. Bakry, I. Feuerstein, G. Stecher, S. Morandell, H.L. Huang, T. Stasyk, L.A. Huber, and G.K. Bonn. 2005. Poly(glycidyl methacrylate/divinylbenzene)IDA-FeIII in phosphoproteomics. J. Proteome Res. 4: 2312-2319.

Arvidsson, P., F.M. Plieva, V.I. Lozinsky, I.Y. Galaev, and B. Mattiasson. 2003. Direct chromatographic capture of enzyme from crude homogenate using immobilized metal affinity chromatography on a continuous supermacroporous adsorbent. J. Chromatogr. A 986: 275–290.

Arvidsson, P., F.M. Plieva, I.N. Savina, V.I. Lozinsky, S. Fexby, L. Bulow, I.Y. Galaev, and B. Mattiasson. 2002. Chromatography of microbial cells using continuous supermacroporous affinity and ion-exchange columns. J. Chromatogr. A 977: 27–38.

Bhattacharyya, A. and C.M. Klapperich. 2008. Microfluidics-based extraction of viral RNA from infected mammalian cells for disposable molecular diagnostics. Sens. Actuators B: Chem. 129: 693–698.

Bisjak, C.P., R. Bakry, C.W. Huck, and G.K. Bonn. 2005. Amino-functionalized monolithic poly(glycidyl methacrylate-co-divinylbenzene) ion-exchange stationary phases for the separation of oligonucleotides. Chromatographia 62: s31–s36.

Branovic, K., D. Forcic, J. Ivancic, A. Strancar, M. Barut, T. Kosutic Gulija, R. Zgorelec, and R. Mazuran. 2004. Application of short monolithic columns for fast purification of plasmid DNA. J. Chromatogr. B: Analyt. Technol. Biomed. Life Sci. 801: 331–337.

Brne, P., A. Podgornik, K. Bencina, B. Gabor, A. Strancar, and M. Peterka. 2007. Fast and efficient separation of immunoglobulin M from immunoglobulin G using short monolithic columns. J. Chromatogr. A 1144: 120–125.

Cabrera, K. 2004. Applications of silica-based monolithic HPLC columns. J. Sep. Sci. 27: 843–852.

Chatterjee, A., P.L. Mirer, E. Zaldivar Santamaria, C. Klapperich, A. Sharon, and A.F. Sauer-Budge. 2010. RNA isolation from mammalian cells using porous polymer monoliths: An approach for high-throughput automation. Anal. Chem. 82: 4344–4356.

Costioli, M.D., I. Fisch, F. Garret-Flaudy, F. Hilbrig, and R. Freitag. 2003. DNA purification by triple-helix affinity precipitation. Biotechnol. Bioeng. 81: 535–545.

Crooke, S.T. 1998. Antisense Research and Application. Berlin, Germany: Springer.

Dainiak, M.B., I.Y. Galaev, A. Kumar, F.M. Plieva, and B. Mattiasson. 2007a. Chromatography of living cells using supermacroporous hydrogels, cryogels. Adv. Biochem. Eng. Biotechnol. 106: 101–127.

Dainiak, M.B., I.Y. Galaev, and B. Mattiasson. 2006a. Affinity cryogel monoliths for screening for optimal separation conditions and chromatographic separation of cells. J. Chromatogr. A 1123: 145–150.

Dainiak, M.B., I.Y. Galaev, and B. Mattiasson. 2007b. Macroporous monolithic hydrogels in a 96-minicolumn plate format for cell surface-analysis and integrated binding/quantification of cells. Enzyme Microb. Technol. 40: 688–695.

Dainiak, M.B., A. Kumar, I.Y. Galaev, and B. Mattiasson. 2006b. Detachment of affinitycaptured bioparticles by elastic deformation of a macroporous hydrogel. Proc. Natl. Acad. Sci. USA 103: 849–854.

Dainiak, M.B., A. Kumar, F.M. Plieva, I.Y. Galaev, and B. Mattiasson. 2004. Integrated isolation of antibody fragments from microbial cell culture fluids using supermacroporous cryogels. J. Chromatogr. A 1045: 93–98.

Dainiak, M.B., F.M. Plieva, I.Y. Galaev, R. Hatti-Kaul, and B. Mattiasson. 2005. Cell chromatography: Separation of different microbial cells using IMAC supermacroporous monolithic columns. Biotechnol. Prog. 21: 644–649.

Dainiak, M.B., I.N. Savina, I. Musolino, A. Kumar, B. Mattiasson, and I.Y. Galaev. 2008. Biomimetic macroporous hydrogel scaffolds in a high-throughput screening format for cell-based assays. Biotechnol. Prog. 24: 1373–1383.

Forcic, D., K. Branovic-Cakanic, J. Ivancic, R. Jug, M. Barut, and A. Strancar. 2005. Purification of genomic DNA by short monolithic columns. J. Chromatogr. A 1065: 115–120.

Freitag, R. and S. Vogt. 2000. Comparison of particulate and continuous-bed columns for protein displacement chromatography. J. Biotechnol. 78: 69–82.

Gilar, M. and E.S.P. Bouvier. 2000. Purification of crude DNA oligonucleotides by solid-phase extraction and reversed-phase high-performance liquid chromatography. J. Chromatogr. A 890: 167–177.

Hanora, A., I. Savina, F.M. Plieva, V.A. Izumrudov, B. Mattiasson, and I.Y. Galaev. 2006. Direct capture of plasmid DNA from non-clarified bacterial lysate using polycationgrafted monoliths. J. Biotechnol. 123: 343–355.

Holdsvendova, P., J. Suchankova, M. Buncek, V. Backovska, and P. Coufal. 2007. Hydroxymethyl methacrylate-based monolithic columns designed for separation of oligonucleotides in hydrophilic-interaction capillary liquid chromatography. J. Biochem. Biophys. Methods 70: 23–29.

Hoth, D.C., J.G. Rivera, and L.A. Colon. 2005. Metal oxide monolithic columns. J. Chromatogr. A 1079: 392–396.

Huber, C.G. 1998. Micropellicular stationary phases for high-performance liquid chromatography of double-stranded DNA. J. Chromatogr. A 806: 3–30.

Ikegami, T., E. Dicks, H. Kobayashi, H. Morisaka, D. Tokuda, K. Cabrera, K. Hosoya, and N. Tanaka. 2004. How to utilize the true performance of monolithic silica columns. J. Sep. Sci. 27: 1292–1302.

Isobe, K. and Y. Kawakami. 2007. Preparation of convection interaction media isobutyl disc monolithic column and its application to purification of secondary alcohol dehydrogenase and alcohol oxidase. J. Chromatogr. A 1144: 85–89.

Josic, D. and J. Clifton. 2007. Use of monolithic supports in proteomics technology. J. Chromatogr. A 1144: 2–13.

Jungbauer, A. and R. Hahn. 2004. Monoliths for fast bioseparation and bioconversion and their applications in biotechnology. J. Sep. Sci. 27: 767–778.

Krajacic, M., J. Ivancic-Jelecki, D. Forcic, A. Vrdoljak, and D. Skoric. 2007. Purification of plant viral and satellite double-stranded RNAs on DEAE monoliths. J. Chromatogr. A 1144: 111–119.

Kumar, A., V. Bansal, J. Andersson, P.K. Roychoudhury, and B. Mattiasson. 2006. Supermacroporous cryogel matrix for integrated protein isolation. Immobilized metal affinity chromatographic purification of urokinase from cell culture broth of a human kidney cell line. J. Chromatogr. A 1103: 35–42.

Kumar, A., I.Y. Galaev, and B. Mattiasson. 2007. Cell Separation: Fundamentals, Analytical and Preparative Methods. Berlin, Germany: Springer-Verlag.

Kumar, A., F.M. Plieva, I.Y. Galaev, and B. Mattiasson. 2003. Affinity fractionation of lymphocytes using a monolithic cryogel. J. Immunol. Methods 283: 185–194.

Kumar, A., A. Rodriguez-Caballero, F.M. Plieva, I.Y. Galaev, K.S. Nandakumar, M. Kamihira, R. Holmdahl, A. Orfao, and B. Mattiasson. 2005. Affinity binding of cells to cryogel adsorbents with immobilized specific ligands: Effect of ligand coupling and matrix architecture. J. Mol. Recognit. 18: 84–93.

Kumar, A. and A. Srivastava. 2010. Cell separation using cryogel-based affinity chromatography. Nat. Protoc. 5: 1737–1747.

Leinweber, F.C. and U. Tallarek. 2003. Chromatographic performance of monolithic and particulate stationary phases. Hydrodynamics and adsorption capacity. J. Chromatogr. A 1006: 207–228.

Lesignoli, E., A. Germini, R. Corradini, S. Sforza, G. Galavema, A. Dossena, and R. Marchelli. 2001. Recognition and strand displacement of DNA oligonucleotides by peptide nucleic acids (PNAs). High-performance ion-exchange chromatographic analysis. J. Chromatogr. A 922: 177–185.

Levkin, P.A., S. Eeltink, T.R. Stratton, R. Brennen, K. Robotti, H. Yin, K. Killeen, F. Svec, and J.M. Frechet. 2008. Monolithic porous polymer stationary phases in polyimide chips for the fast high-performance liquid chromatography separation of proteins and peptides. J. Chromatogr. A 1200: 55–61.

Li, Y. and M.L. Lee. 2009. Biocompatible polymeric monoliths for protein and peptide separations. J. Sep. Sci. 32: 3369–3378.

Li, Y.M., J.L. Liao, K. Nakazato, J. Mohammad, L. Terenius, and S. Hjerten. 1994. Continuous beds for microchromatography: Cation-exchange chromatography. Anal. Biochem. 223: 153–158.

Liang, C., S. Dai, and G. Guiochon. 2003. A graphitized-carbon monolithic column. Anal. Chem. 75: 4904–4912.

Liao, J.-L., R. Zhang, and S. Hjerten. 1991. Continuous beds for standard and micro highperformance liquid chromatography. J. Chromatogr. A 586: 21–26.

Lin, L., H. Chen, H. Wei, F. Wang, and J.M. Lin. 2011. On-chip sample pretreatment using a porous polymer monolithic column for solid-phase microextraction and chemiluminescence determination of catechins in green tea. Analyst 136: 4260–4267.

Lin, Z., H. Huang, X. Sun, Y. Lin, L. Zhang, and G. Chen. 2012. Monolithic column based on a poly(glycidyl methacrylate-co-4-vinylphenylboronic acid-co-ethylene dimethacrylate) copolymer for capillary liquid chromatography of small molecules and proteins. J. Chromatogr. A 1246: 90–97.

Lozinsky, V.I. 2002. Cryogels on the basis of natural and synthetic polymers: Preparation, properties and application. Uspekhi. Khimii. 71: 559–585.

Lozinsky, V.I., I.Y. Galaev, F.M. Plieva, I.N. Savina, H. Jungvid, and B. Mattiasson. 2003. Polymeric cryogels as promising materials of biotechnological interest. Trends Biotechnol. 21: 445–451.

Luo, Q., Y. Shen, K.K. Hixson, R. Zhao, F. Yang, R.J. Moore, H.M. Mottaz, and R.D. Smith. 2005. Preparation of 20-microm-i.d. silica-based monolithic columns and their performance for proteomics analyses. Anal. Chem. 77:

5028–5035.

Luo, Q., H. Zou, Q. Zhang, X. Xiao, and J. Ni. 2002. High-performance af�nity chromatography with immobilization of protein A and l-histidine on molded monolith. Biotechnol. Bioeng. 80: 481–489.

Ma, J., L. Zhang, Z. Liang, W. Zhang, and Y. Zhang. 2007. Monolith-based immobilized enzyme reactors: Recent developments and applications for proteome analysis. J. Sep. Sci. 30: 3050–3059.

Malvy, C., A. Harel-Bellan, and L.L. Pritchard. 1999. Triple Helix Forming Oligonucleotides. Springer, New York.

Miller, S. 2004. Separations in a monolith. Anal. Chem. 76: 99–101.

Minakuchi, H., K. Nakanishi, N. Soga, N. Ishizuka, and N. Tanaka. 1996. Octadecylsilylated porous silica rods as separation media for reversed-phase liquid chromatography. Anal. Chem. 68: 3498–3501.

Minakuchi, H., K. Nakanishi, N. Soga, N. Ishizuka, and N. Tanaka. 1998. Effect of domain size on the performance of octadecylsilylated continuous porous silica columns in reversed-phase liquid chromatography. J. Chromatogr. A 797: 121–131.

Miyamoto, K., T. Hara, H. Kobayashi, H. Morisaka, D. Tokuda, K. Horie, K. Koduki et al. 2008. High-ef�ciency liquid chromatographic separation utilizing long monolithic silica capillary columns. Anal. Chem. 80: 8741–8750.

Motokawa, M., H. Kobayashi, N. Ishizuka, H. Minakuchi, K. Nakanishi, H. Jinnai, K. Hosoya, T. Ikegami, and N. Tanaka. 2002. Monolithic silica columns with various skeleton sizes and through-pore sizes for capillary liquid chromatography. J. Chromatogr. A 961: 53–63.

Nawrocki, J., C. Dunlap, J. Li, J. Zhao, C.V. McNeffe, A. McCormick, and P.W. Carr. 2004a. Part II. Chromatography using ultra-stable metal oxide-based stationary phases for HPLC. J. Chromatogr. A 1028: 31–62.

Nawrocki, J., C. Dunlap, A. McCormick, and P.W. Carr. 2004b. Part I. Chromatography using ultra-stable metal oxide-based stationary phases for HPLC. J. Chromatogr. A 1028: 1–30.

Nordborg, A., E.F. Hilder, and P.R. Haddad. 2011. Monolithic phases for ion chromatography. Annu. Rev. Anal. Chem. (Palo Alto Calif.) 4: 197–226.

Oberacher, H., A. Krajete, W. Parson, and C.G. Huber. 2000. Preparation and evaluation of packed capillary columns for the separation of nucleic acids by ion-pair reversed-phase high-performance liquid chromatography. J. Chromatogr. A 893: 23–35.

Ostryanina, N.D., G.P. Vlasov, and T.B. Tennikova. 2002. Multifunctional fractionation of polyclonal antibodies by immunoaffinity high-performance monolithic disk chromatography. J. Chromatogr. A 949: 163–171.

Padmapriya, A.A., J. Tang, and S. Agrawal. 1994. Large-scale synthesis, purification, and analysis of oligodeoxynucleotide phosphorothioates. Antisense Res. Dev. 4: 185–199.

Perica, M.C., I. Sola, L. Urbas, F. Smrekar, and M. Krajacic. 2009. Separation of hypoviral double-stranded RNA on monolithic chromatographic supports. J. Chromatogr. A 1216: 2712–2716.

Peterka, M., M. Jarc, M. Banjac, V. Frankovic, K. Bencina, M. Merhar, V. Gaberc-Porekar, V. Menart, A. Strancar, and A. Podgornik. 2006. Characterisation of metal-chelate methacrylate monoliths. J. Chromatogr. A 1109: 80–85.

Plieva, F., H.T. Xiao, I.Y. Galaev, B. Bergenstahl, and B. Mattiasson. 2006. Macroporous elastic polyacrylamide gels prepared at subzero temperatures: Control of porous structure. J. Mater. Chem. 16: 4065–4073.

Plieva, F.M., I.Y. Galaev, and B. Mattiasson. 2007. Macroporous gels prepared at subzero temperatures as novel materials for chromatography of particulate-containing uids and cell culture applications. J. Sep. Sci. 30: 1657–1671.

Plieva, F.M., M. Karlsson, M.-R. Aguilar, D. Gomez, S. Mikhalovsky, and I.Y. Galaev. 2005. Pore structure in supermacroporous polyacrylamide based cryogels. Soft Matter 1: 303–309.

Podgornik, A. and A. Strancar. 2005. Convective Interaction Media (CIM)—Short layer monolithic chromatographic stationary phases. Biotechnol. Annu. Rev. 11: 281–333.

Qiu, R. and F.E. Regnier. 2005. Use of multidimensional lectin affinity chromatography in differential glycoproteomics. Anal. Chem. 77: 2802–2809.

Rucevic, M., J. Clifton, F. Huang, X. Li, H. Callanan, D.C. Hixson, and D. Josic. 2006. Use of short monolithic columns for isolation of low abundance membrane proteins. J. Chromatogr. A 1123: 199–204.

Satterfield, B.C., S. Stern, M.R. Caplan, K.W. Hukari, and J.A. West. 2007. Microfluidic purification and preconcentration of mRNA by flow-through polymeric monolith. Anal. Chem. 79: 6230–6235.

Smått, J.H., F.M. Sayler, A.J. Grano, and M.G. Bakker. 2012. Formation of hierarchically porous metal oxide and metal monoliths by nanocasting into silica monoliths. Adv. Eng. Mater. 14: 1059–1073.

Smått, J.H., C. Weidenthaler, J.B. Rosenholm, and M. Lindén. 2006. Hierarchically porous metal oxide monoliths prepared by the nanocasting route. Chem. Mater. 18: 1443–1450.

Srivastava, A., A.K. Shakya, and A. Kumar. 2012. Boronate affinity chromatography of cells and biomacromolecules using cryogel matrices. Enzyme Microb. Technol. 51: 373–381.

Strancar, A., M. Barut, A. Podgornik, P. Koselj, H. Schwinn, P. Raspor, and D. Josic. 1997. Application of compact porous tubes for preparative isolation of clotting factor VIII from human plasma. J. Chromatogr. A 760: 117–123.

Strancar, A., A. Podgornik, M. Barut, and R. Necina. 2002. Advances in Biochemical Engineering/Biotechnology. Heidelberg, Germany: Springer-Verlag.

Svec, F. and J.M.J. Fréchet. 1992. Continuous rods of macroporous polymer as highperformance liquid chromatography separation media. Anal. Chem. 64: 820–822.

Svec, F. and C.G. Huber. 2006. Monolithic materials: Promises, challenges, achievements. Anal. Chem. 78: 2101–2107.

Taguchi, A., J.-H. Smått, and M. Lindén. 2003. Carbon monoliths possessing a hierarchical, fully interconnected porosity. Adv. Mater. 15: 1209–1211.

Tanaka, N., H. Kobayashi, K. Nakanishi, H. Minakuchi, and N. Ishizuka. 2001. Monolithic LC columns. Anal. Chem. 73: 420A–429A.

Teeters, M.A., S.E. Conrardy, B.L. Thomas, T.W. Root, and E.N. Lightfoot. 2003. Adsorptive membrane chromatography for puriﬁcation of plasmid DNA. J. Chromatogr. A 989: 165–173.

Teilum, M., M.J. Hansson, M.B. Dainiak, R. Mansson, S. Surve, E. Elmer, P. Onnerfjord, and G. Mattiasson. 2006. Binding mitochondria to cryogel monoliths allows detection of proteins speciﬁcally released following permeability transition. Anal. Biochem. 348: 209–221.

Toll, H., R. Wintringer, U. Schweiger-Hufnagel, and C.G. Huber. 2005. Comparing monolithic and microparticular capillary columns for the separation and analysis of peptide mixtures by liquid chromatography-mass spectrometry. J. Sep. Sci. 28: 1666–1674.

Tong, S., Q. Liu, Y. Li, W. Zhou, Q. Jia, and T. Duan. 2012. Preparation of porous polymer monolithic column incorporated with graphene nanosheets for solid phase microextraction and enrichment of glucocorticoids. J. Chromatogr. A 1253: 22–31.

Unger, K.K., R. Skudas, and M.M. Schulte. 2008. Particle packed columns and monolithic columns in high-performance liquid chromatography-comparison and critical appraisal. J. Chromatogr. A 1184: 393–415.

Urthaler, J., R. Schlegl, A. Podgornik, A. Strancar, A. Jungbauer, and R. Necina. 2005. Application of monoliths for plasmid DNA puriﬁcation development and transfer to production. J. Chromatogr. A 1065: 93–106.

Vlakh, E.G. and T.B. Tennikova. 2009. Applications of polymethacrylate-based monoliths in high-performance liquid chromatography. J. Chromatogr. A 1216: 2637–2650.

Wang, Q.C., F. Svec, and J.M. Frechet. 1993. Macroporous polymeric stationary-phase rod as continuous separation medium for reversed-phase chromatography. Anal. Chem. 65: 2243–2248.

Weith, H.L., J.L. Wiebers, and P.T. Gilham. 1970. Synthesis of cellulose derivatives containing the dihydroxyboryl group and a study of their capacity to form speciﬁc complexes with sugars and nucleic acid components. Biochemistry 9: 4396–4401.

Williams, S.L., M.E. Eccleston, and N.K. Slater. 2005. Affinity capture of a biotinylated retrovirus on macroporous monolithic adsorbents: Towards a rapid single-step purification process. Biotechnol. Bioeng. 89: 783–787.

Wu, Q., J.M. Bienvenue, B.J. Hassan, Y.C. Kwok, B.C. Giordano, P.M. Norris, J.P. Landers, and J.P. Ferrance. 2006. Microchip-based macroporous silica sol-gel monolith for efficient isolation of DNA from clinical samples. Anal. Chem. 78: 5704–5710.

Wuhrer, M., C.A. Koeleman, C.H. Hokke, and A.M. Deelder. 2005. Protein glycosylation analyzed by normal-phase nano-liquid chromatography—Mass spectrometry of glycopeptides. Anal. Chem. 77: 886–894.

Xu, H., S. Wang, G. Zhang, S. Huang, D. Song, Y. Zhou, and G. Long. 2011. A novel solid-phase microextraction method based on polymer monolith frit combining with high-performance liquid chromatography for determination of aldehydes in biological samples. Anal. Chim. Acta 690: 86–93.

Xu, Y., Q. Cao, F. Svec, and J.M. Frechet. 2010. Porous polymer monolithic column with surface-bound gold nanoparticles for the capture and separation of cysteine-containing peptides. Anal. Chem. 82: 3352–3358.

Xu, Z. and R.D. Oleschuk. 2014. A fluorous porous polymer monolith photo-patterned chromatographic column for the separation of a flourous/fluorescently labeled peptide within a microchip. Electrophoresis. 35: 441–449.

Yamamoto, S., M. Nakamura, C. Tarmann, and A. Jungbauer. 2007. Retention studies of DNA on anion-exchange monolith chromatography binding site and elution behavior. J. Chromatogr. A 1144: 155–160.

Zochling, A., R. Hahn, K. Ahrer, J. Urthaler, and A. Jungbauer. 2004. Mass transfer characteristics of plasmids in monoliths. J. Sep. Sci. 27: 819–827.

4 Chapter 4: Polysaccharide-Based Composite Hydrogels for Removal of Pollutants from Water

An, J.K., W.B. Wang, and A.Q. Wang. 2010. Preparation and swelling properties of a pH-sensitive superabsorbent hydrogel based on psyllium gum. Starch/Stärke 62: 501–507.

An, J.K., W.B. Wang, and A.Q. Wang. 2011a. Preparation and swelling properties of ph responsive psyllium-graft-poly(acrylic acid)/biotite superabsorbent composites. Polym. Mater. Sci. Eng. 27: 31–34.

An, J.K., W.B. Wang, and A.Q. Wang. 2011b. Preparation of psyllium gum-g-poly(acrylic acid)/Na-montmorillonite supersorbent composites and its adsorption performance for Cu 2+ . J. Funct. Polym. 24: 186–190.

An, J.K., W.B. Wang, and A.Q. Wang. 2012. Preparation and swelling behavior of a pHresponsive psyllium-g-poly(acrylic acid)/attapulgite superabsorbent nanocomposite. Int. J. Polym. Mater. 61: 906–918.

Borggaard, O.K., B. Raben-Lange, A.L. Gimsing, and B.W. Strobel. 2005. In�uence of humic substances on phosphate adsorption by aluminium and iron oxides. Geoderma 127: 270–279.

Bradley, W.F. 1940. The structural scheme of attapulgite. Am. Miner. 25: 405–410.

Chen, H., W.B. Wang, and A.Q. Wang. 2010. Preparation and swelling behaviors of CMCg-PAA/APT/HA superabsorbent composites. Humic Acid 5: 5–10.

Chen, H., Y.G. Zhao, and A.Q. Wang. 2007. Removal of Cu(II) from aqueous solution by adsorption onto acid-activated palygorskite. J. Hazard. Mater. 149: 346–354.

Chen, H.B., Y.T. Wang, M. Sánchez-Sotoc, and D.A. Schiraldi. 2012. Low �ammability, foamlike materials based on ammonium alginate and sodium montmorillonite clay. Polymer 53: 5825–5831.

Chen, X.B., J.V. Wright, J.L. Conca, and L.M. Peurrung. 1997. Effects of pH on heavy metal sorption on mineral apatite. Environ. Sci. Technol. 31: 624–631.

Chivrac, F., E. Pollet, M. Schmutz, and L. Avérous. 2008. New approach to elaborate exfoliated starch-based nanobiocomposites. Biomacromolecules 9: 896-900.

Dawson, J.I., J.M. Kanczler, X.B.B. Yang, G.S. Attard, and R.O.C. Oreffo. 2011. Skeletal regeneration: Application of nanotopography and biomaterials for skeletal stem cell based bone repair. Adv. Mater. 23: 3304–3308.

Deen, I., X. Pang, and I. Zhitomirsky. 2012. Electrophoretic deposition of composite chitosan-halloysite nanotube-hydroxyapatite films. Colloids Surf. A 410: 38–44.

Demirbas, A. 2008. Heavy metal adsorption onto agro-based waste materials: A review. J. Hazard. Mater. 157: 220–229.

Drizo, A., C.A. Frost, K.A. Smith, and J. Grace. 1998. Phosphate and ammonium removal by constructed wetlands with horizontal subsurface flow, using shale as a substrate. Water Res. 35: 95–102.

Gao, H.C., Y.M. Sun, J.J. Zhou, R. Xu, and H.W. Duan. 2013. Mussel-inspired synthesis of polydopamine-functionalized graphene hydrogel as reusable adsorbents for water purification. ACS Appl. Mater. Interfaces 5: 425–432.

Gao, T.P., W.B. Wang, and A.Q. Wang. 2011. A pH-sensitive composite hydrogel based on sodium alginate and medical stone: Synthesis, swelling and heavy metal ions adsorption properties. Macromol. Res. 19: 739–748.

Hayes, M.H.B., P. MacCarthy, R.L. Malcolm, and R.S. Swift (eds.). Humic Substances II: In Search of Structure. Chichester, U.K.: Wiley; 1989.

Hua, S.B. and A.Q. Wang. 2008. Preparation and properties of superabsorbent containing starch and sodium humate. Polym. Adv. Technol. 19: 1009–1014.

Hua, S.B., H.X. Yang, and A.Q. Wang. 2008. A pH-sensitive nanocomposite microsphere based on chitosan and montmorillonite with in vitro reduction of the burst release effect. Drug Dev. Ind. Pharm. 36: 1106–1114.

Hua, S.B., H.X. Yang, W.B. Wang, and A.Q. Wang. 2010. Controlled release of ofloxacin from chitosan-montmorillonite hydrogel. Appl. Clay Sci. 50: 112–117.

Hua, S.B., H.X. Yang, J.P. Zhang, and A.Q. Wang. 2012. Preparation and swelling properties of pH-sensitive sodium alginate/layered double hydroxides hybrid beads for controlled release of diclofenac sodium. Drug Dev. Ind. Pharm. 38: 728–734.

Huang, D.J., B. Mu, and A.Q. Wang. 2012a. Preparation and properties of chitosan/poly (vinyl alcohol) nanocomposite lms reinforced with rod-like sepiolite. Mater. Lett. 86: 69–72.

Huang, W., H.J.L. Xu, Y. Xue, R. Huang, H.B. Deng, and S.Y. Pan. 2012b. Layer-by-layer immobilization of lysozome-chitosan-organic rectorite composites on electrospun nano�brous mats for pork preservation. Food Res. Int. 48: 784–791.

Huang, Y.S., S.H. Yu, Y.R. Sheu, and K.S. Huang. 2010. Preparation and thermal and anti-UV properties of chitosan/mica copolymer. J. Nanomater. 2010: 65–71.

Juan, L., P.Y. Zhang, Y. Gao, X.G. Song, and J.H. Dong. 2008. Overview of Maifanshi: Its physi-chemical properties and nutritious function in drinking water. Environ. Sci. Technol. 31: 63–67.

Klien, C., B. Dutrow, and J.D. Dana. Manual of Mineral Science, 23rd edn. Hoboken, NJ: John Wiley & Sons, Inc.,; 2008.

Li, A., R.F. Liu, and A.Q. Wang. 2005. Preparation of starch-graft-poly (acrylamide)/attapulgite superabsorbent composite. J. Appl. Polym. Sci. 98: 1351.

Li, A., A.Q. Wang, and J.M. Chen. 2004. Studies on poly(acrylic acid)/attapulgite superabsorbent composite. I. Synthesis and characterization. J. Appl. Polym. Sci. 92: 1596-1603.

Li, A., J.P. Zhang, and A.Q. Wang. 2007a. Utilization of starch and clay for the preparation of superabsorbent composite. Bioresour. Technol. 98: 327–332.

Li, J.F., Y.M. Li, and H.P. Dong. 2008. Controlled release of herbicide acetochlor from clay/ carboxylmethilcellulose gel formulations. J. Agric. Food Chem. 56: 1336–1342.

Li, P., J.P. Zhang, and A.Q. Wang. 2007b. A novel succinyl-chitosan-g-polyacrylamide/ attapulgite composite hydrogel prepared through inverse suspension polymerization. Macromol. Mater. Eng. 292: 962–969.

Li, Q., Y.H. Zhao, L. Wang, and A.Q. Wang. 2011a. Adsorption characteristics of methylene blue onto the N-succinyl-chitosan-g-polyacrylamide/attapulgite composite. Korean J. Chem. Eng. 28: 1658–1664.

Li, X.X., X.Y. Li, B.L. Ke, X.W. Shi, and Y.M. Du. 2011b. Cooperative performance of chitin whisker and rectorite fillers on chitosan films. Carbohydr. Polym. 85: 747–752.

Li, Y., P.R. Chang, P.W. Zheng, and X.F. Ma. 2012a. Characterization of magnetic guar gum-grafted carbon nanotubes and the adsorption of the dyes. Carbohydr. Polym. 87: 1919–1924.

Li, Z.Q., J.F. Shen, H.W. Ma, X. Lu, M. Shi, N. Li, and M.X. Ye. 2012b. Preparation and characterization of sodium alginate/poly(N-isopropylacrylamide)/clay semi-IPN magnetic hydrogels. Polym. Bull. 68: 1153–1169.

Lin, J.M., J.H. Wu, Z.F. Yang, and M.L. Pu. 2001. Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. Macromol. Rapid Commun. 22: 422–424.

Liu, A.D., A. Walther, O. Ikkala, L. Belova, and A. Lars Berglund. 2011a. Clay nanopaper with tough cellulose nanofiber matrix for fire retardancy and gas barrier functions. Biomacromolecules 12: 633–641.

Liu, B., X.Y. Wang, X.Y. Li, X.J. Zeng, R.C. Sun, and J.F. Kennedy. 2012a. Rapid exfoliation of rectorite in quaternized carboxymethyl chitosan. Carbohydr. Polym. 90: 1826–1830.

Liu, B., X.Y. Wang, C.S. Pang, J.W. Luo, Y.Q. Luo, and R.C. Sun. 2013a. Preparation and antimicrobial property of chitosan oligosaccharide derivative/rectorite nanocomposite. Carbohydr. Polym. 92: 1078–1085.

Liu, H., X. Sun, C. Yin, and C. Hu. 2008. Removal of phosphate by mesoporous ZrO_2. J. Hazard. Mater. 151: 616–622.

Liu, J.H. and A.Q. Wang. 2008a. Synthesis & water retention of chitosan-g-poly(acrylic acid)/ rectorite superabsorbent composites. Non-Metallic Mines 31: 37–40.

Liu, J.H. and A.Q. Wang. 2008b. Synthesis, characterization and swelling behaviors of chitosan-g-poly(acrylic acid)/organo-rectorite nanocomposite superabsorbents. J. Appl. Polym. Sci. 110: 678–686.

Liu, J.H., Q. Wang, and A.Q. Wang. 2007. Synthesis and characterization of chitosang-poly(acrylic acid)/sodium humate superabsorbent. Carbohydr. Polym. 70: 166–173.

Liu, Y., H. Chen, J.P. Zhang, and A.Q. Wang. 2013b. Effect of number of grindings of attapulgite on enhanced swelling properties of the superabsorbent nanocomposites. J. Compos. Mater. 47: 969–978.

Liu, Y., Y.R. Kang, D.J. Huang, and A.Q. Wang. 2012b. Cu 2+ removal from aqueous solution by modi�ed chitosan hydrogels. J. Chem. Technol. Biotechnol. 87: 1010–1016.

Liu, Y., W.B. Wang, Y.L. Jin, and A.Q. Wang. 2011b. Adsorption behavior of methylene blue from aqueous solution on the hydrogel composites based on carboxymethyl cellulose and attapulgite. Sep. Sci. Technol. 46: 858–868.

Liu, Y., W.B. Wang, and A.Q. Wang. 2010a. Adsorption of lead ions from aqueous solution by using carboxymethyl cellulose-g-poly (acrylic acid)/attapulgite hydrogel composites. Desalination 259: 258–264.

Liu, Y., Y.A. Zheng, and A.Q. Wang. 2010b. Enhanced adsorption of methylene blue from aqueous solution by chitosan-g-poly (acrylic acid)/vermiculite hydrogel composites. J. Environ. Sci. 22: 486–493.

Liu, Y., Y.A. Zheng, and A.Q. Wang. 2011c. Effect of biotite of hydrogels on enhanced removal of cationic dye from aqueous solution. Ionics 17: 535–543.

Liu, Y., Y.A. Zheng, and A.Q. Wang. 2011d. Response surface methodology for optimizing adsorption process parameters for methylene blue removal by hydrogel composite. Adsorpt. Sci. Technol. 28: 913–922.

Luo, W., W.A. Zhang, and P. Chen. 2005. Co-(acrylic acid)/montmorillonite nanosuperabsorbent via gamma-ray irradiation technique. J. Appl. Polym. Sci. 96: 1341–1346.

Lutolf, M.P. and J.A. Hubbell. 2005. Synthetic biomaterials as instructive extracellular microenvironments for morphogenesis in tissue engineering. Nat. Biotechnol. 23: 47–55.

Ma, J.H., Y.J. Xu, Q.S. Zhang, L.S. Zha, and B. Liang. 2007. Preparation and characterization of pH- and temperature-responsive semi-IPN hydrogels of carboxymethyl chitosan with poly(N-isopropylacrylamide) crosslinked by clay. Colloid Polym. Sci. 285: 479–484.

Ma, J.H., L. Zhang, B. Fan, Y.J. Xu, and B.R. Liang. 2008. A novel sodium carboxymethylcellulose/poly(N-isopropylacrylamide)/clay semi-IPN nanocomposite hydrogel with improved response rate and mechanical properties. J. Polym. Sci. Part B: Polym. Phys. 46: 1546–1555.

Marandi, G.B., G.R. Mahdavinia, and S. Ghafary. 2011. Collagen-g-poly(sodium acrylateco-acrylamide)/sodium montmorillonite superabsorbent nanocomposites: Synthesis and swelling behavior. J. Polym. Res. 18: 1487–1499.

Margarita, D., L.B. Mar, A. Pilar, J.A. Antonio, B. Julio, and R.H. Eduardo. 2006. Microfibrous chitosan-sepiolite nanocomposites. Chem. Mater. 18: 1602–1610.

Margarita, D., C. Montserrat, and R.H. Eduardo. 2003. Biopolymer-clay nanocomposites based on chitosan intercalated in montmorillonite. Chem. Mater. 15: 3774–3780.

Neaman, A. and A. Singer. 2004. Possible use of the Sacalum (Yucatan) palygorskite as drilling muds. Appl. Clay Sci. 25: 121–124.

Ni, B.L., M.Z. Liu, S.Y. Lü, L.H. Xie, and Y.F. Wang. 2011. Environmentally friendly slowrelease nitrogen fertilizer. J. Agric. Food Chem. 59: 10169–10175.

Peng, X.W., L.X. Zhong, J.L. Ren, and R.C. Sun. 2012. Synthesis and characterization of amphoteric xylan-type hemicelluloses by microwave irradiation. J. Agric. Food Chem. 60: 3909–3916.

Perotti, G.F., H.S. Barud, Y. Messaddeq, S.J.L. Ribeiro, and R.L. Constantino Vera. 2011. Bacterial cellulose–laponite clay nanocomposites. Polymer 52: 157–163.

Ray, S.S. and M. Okamoto. 2003. Polymer/layered silicate nanocomposites: Structure formation, interactions and deformation mechanisms. Prog. Polym. Sci. 28: 1539–1641.

Reza, M.G., M. Abdolhossein, B. Ali, and M. Bakhshali. 2012a. Novel carrageenan-based hydrogel nanocomposites containing laponite RD and their application to remove cationic dye. Iran. Polym. J. 21: 609–619.

Saad, R., K. Belkacemi, and S. Hamoudi. 2007. Adsorption of phosphate and nitrate anions on ammonium-functionalised MCM-48: Effects of experimental conditions. J. Colloid Interface Sci. 311: 375–381.

Sakadevan, K. and H. Bavor. 1998. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. Water Res. 32: 393–398.

Shang, J., Z.Z. Shao, and X. Chen. 2008. Electrical behavior of a natural polyelectrolyte hydrogel: Chitosan/carboxymethylcellulose hydrogel. Biomacromolecules 9: 1208–1213.

Shchukin, D.G., S.V. Lamaka, K.A. Yasakau, M.L. Zheludkevich, M.G.S. Ferreira, and H. Möhwald. 2008. Active anticorrosion coatings with halloysite nanocontainers. J. Phys. Chem. C 112: 958–964.

Shi, J.W. 2011. Synthesis and adsorption performance of CTS-g-poly(acrylic acid)/ sepiolite composites. Master’s thesis, Chengdu University of Technology, Chengdu, China, p. 6.

Shi, X.N. and A.Q. Wang. 2011. Synthesis and swelling properties of guar gum-g-poly(sodium acrylate-co-styrene)/sepiolite superabsorbent composite. J. Chem. Ind. Eng. 62: 864–869.

Shi, X.N, W.B. Wang, Y.R. Kang, and A.Q. Wang. 2012. Enhanced swelling properties of a novel sodium alginate-based superabsorbent composites: NaAlg-g-poly(NaA-co-St)/APT. J. Appl. Polym. Sci. 125: 1822–1832.

Shi, X.N., W.B. Wang, and A.Q. Wang. 2011a. Effect of surfactant on porosity and swelling behaviors of guar gum-g-poly(sodium acrylate-co-styrene)/attapulgite superabsorbent hydrogels. Colloids Surf. B 88: 279–286.

Shi, X.N., W.B. Wang, and A.Q. Wang. 2011b. Swelling behavior of guar gum-g-poly(sodium acrylate-co-styrene)/attapulgite superabsorbent composites. J. Macromol. Sci. B 50: 1847–1863.

Shi, X.N., W.B. Wang, and A.Q. Wang. 2011c. Synthesis and enhanced swelling properties of a guar gum-based superabsorbent composite by the simultaneous introduction of styrene and attapulgite. J. Polym. Res. 18: 1705–1713.

Shi, X.N, W.B. Wang, and A.Q. Wang. 2011d. Synthesis, characterization and swelling behaviors of guar gum-g-poly(sodium acrylate-co-styrene)/vermiculite superabsorbent composites. J. Compos. Mater. 45: 2189–2198.

Shi, X.N., W.B. Wang, and A.Q. Wang. 2013. pH-responsive sodium alginate-based superporous hydrogel generated by an anionic surfactant micelle templating. Carbohydr. Polym. 94: 449–455.

Singh, B. and V. Sharma. 2010. Design of psyllium-PVA-acrylic acid based novel hydrogels for use in antibiotic drug delivery. Int. J. Pharm. 389: 94–106.

Singh, V., S. Pandey, S.K. Singh, and R. Sanghi. 2009. Removal of cadmium from aqueous solutions by adsorption using poly(acrylamide) modified guar gum–silica nanocomposites. Sep. Purif. Technol. 67: 251–261.

Sun, J.Y., X. Zhao, W.R. Illeperuma, O. Chaudhuri, K.H. Oh, D.J. Mooney, J.J. Vlassak, and Z. Suo. 2012. Highly stretchable and tough hydrogels. Nature 489: 133–136.

Taleb, M.F.A., G.A. Mahmoud, S.M. Elsigeny, and E.A. Hegazy. 2008. Adsorption and desorption of phosphorus and nitrate ions using quaternary (polypropylene-g-N,Ndimethylaminoethyl methacrylate) graft copolymer. J. Hazard. Mater. 159: 372–379.

Tekin, N., A. Dinçer, Ő. Demirbaş, and M. Alkan. 2006. Adsorption of cation polyacrylamide onto sepiolite. J. Hazard. Mater. B134: 211–219.

Teramoto, N., D. Uchiumi, A. Niikura, Y. Someya, and M. Shibata. 2007. Polypeptide/layered silicate nanocomposites using fish-based collagen peptide: Effect of crosslinking and chain extension of the collagen peptide. J. Appl. Polym. Sci. 106: 4024–4030.

Wang, A.Q. and W.B. Wang. 2009a. Superabsorbent materials. Kirk-Othmer Encyclopedia of Chemical Technology. Wiley, New York, pp. 1–34.

Wang, J.L., W.B. Wang, and A.Q. Wang. 2010a. Synthesis, characterization and swelling behaviors of hydroxyethyl cellulose-g-poly(acrylic acid)/attapulgite superabsorbent composite. Polym. Eng. Sci. 50: 1019–1027.

Wang, J.L., W.B. Wang, Y.A. Zheng, and A.Q. Wang. 2011a. Effects of modified vermiculite on the synthesis and swelling behaviors of hydroxyethyl cellulose-g-poly(acrylic acid)/ vermiculite superabsorbent nanocomposites. J. Polym. Res. 18: 401–408.

Wang, L. and A.Q. Wang. 2008. Adsorption behaviors of Congo red on the N, O-carboxymethylchitosan/montmorillonite nanocomposite. Chem. Eng. J. 143: 43–50.

Wang, L., J.P. Zhang, and A.Q. Wang. 2008a. Removal of methylene blue from aqueous solution using chitosan-g-poly(acrylic acid)/montmorillonite superadsorbent nanocomposite. Colloids Surf. A. 322: 47–53.

Wang, L., J.P. Zhang, and A.Q. Wang. 2011b. Fast removal of methylene blue from aqueous solution by adsorption onto chitosan-g-poly (acrylic acid)/attapulgite composite. Desalination 266: 33–39.

Wang, Q., W.B. Wang, J. Wu, and A.Q. Wang. 2012a. Effect of attapulgite contents on release behaviors of a pH sensitive carboxymethyl cellulose-g-poly (acrylic acid)/attapulgite/ sodium alginate composite hydrogel bead containing diclofenac. J. Appl. Polym. Sci. 124: 4424–4432.

Wang, Q., J. Wu, W.B. Wang, and A.Q. Wang. 2011c. Preparation, characterization and drugrelease behaviors of crosslinked chitosan/attapulgite hybrid microspheres by a facile spray-drying technique. J. Biol. Nanobiotechnol. 2: 250–257.

Wang, Q., X.L. Xie, X.W. Zhang, J.P. Zhang, and A.Q. Wang. 2010b. Preparation and swelling properties of pH sensitive composite hydrogel beads based on chitosan-g-poly (acrylic acid)/vermiculite and sodium alginate for diclofenac controlled release. Int. J. Biol. Macromol. 46: 356–362.

Wang, Q., J.P. Zhang, and A.Q. Wang. 2009a. Preparation and characterization of a novel pHsensitive chitosan-g-poly(acrylic acid)/attapulgite/sodium alginate composite hydrogel bead for controlled release of diclofenac sodium. Carbohydr. Polym. 78: 731–737.

Wang, Q., J.P. Zhang, and A.Q. Wang. 2010c. Preparation and properties of drug loaded hydrogel beads based on halloysite. Chem. Res. Appl. 22: 858–863.

Wang, Q.G., J.L. Mynar, M. Yoshida, E. Lee, M. Lee, K.

Okuro, K. Kinbara, and T. Aida. 2010d. High-water-content mouldable hydrogels by mixing clay and a dendritic molecular binder. Nature 463: 339–343.

Wang, T., D. Liu, C.X. Lian, S.D. Zheng, X.X. Liu, C.Y. Wang, and Z. Tong. 2011d. Rapid cell sheet detachment from alginate semi-interpenetrating nanocomposite hydrogels of PNIPAm and hectorite clay. React. Funct. Polym. 71: 447–454.

Wang, W.B., Y.R. Kang, and A.Q. Wang. 2010e. Synthesis, characterization and swelling properties of the guar gum-g-poly(sodium acrylate-co-styrene)/muscovite superabsorbent composites. Sci. Technol. Adv. Mater. 11: 025006.

Wang, W.B. and A.Q. Wang. 2009b. Effects of crosslinking degree on the properties of guar gumg-poly(acrylic acid)/sodium humate superabsorbents. Polym. Mater. Sci. Eng. 25: 41–44.

Wang, W.B. and A.Q. Wang. 2009c. Preparation and slow released fertilizer properties of GG-g-PAA/SH superabsorbents. Humic Acid 1: 19–23.

Wang, W.B. and A.Q. Wang. 2009d. Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite. Carbohydr. Polym. 77: 891–897.

Wang, W.B. and A.Q. Wang. 2009e. Synthesis and swelling properties of guar gumg-poly(sodium acrylate)/Na-montmorillonite superabsorbent nanocomposite. J. Compos. Mater. 43: 2805–2819.

Wang, W.B. and A.Q. Wang. 2009f. Synthesis, swelling behaviors and slow-release characteristics of guar gum-g-poly(sodium acrylate)/sodium humate superabsorbent. J. Appl. Polym. Sci. 112: 2102–2111.

Wang, W.B. and A.Q. Wang. 2010a. Adsorption and rheological studies of sodium carboxymethyl cellulose onto kaolin: Effect of degree of substitution. Carbohydr. Polym. 82: 83–91.

Wang, W.B. and A.Q. Wang. 2011. Preparation, swelling, and stimuli-responsive characteristics of superabsorbent nanocomposites based on carboxymethyl cellulose and rectorite. Polym. Adv. Technol. 22: 1602–1611.

Wang W.B., J. Wang, Y.R. Kang, and A.Q. Wang. 2011e. Synthesis, swelling and responsive properties of a new composite hydrogel based on hydroxyethyl cellulose and medicinal stone. Composites Part B Eng. 42: 809–818.

Wang, W.B., J. Wang, and A.Q. Wang. 2012b. pH-responsive nanocomposites from methylcellulose and attapulgite nanorods: Synthesis, swelling and absorption performance on heavy metal ions. J. Macromol. Sci. Part A 49: 306–315.

Wang, W.B., J.X. Xu, and A.Q. Wang. 2011f. A pH-, salt- and solvent-responsive carboxymethylcellulose-g-poly(sodium acrylate)/medical stone superabsorbent composite with enhanced swelling and responsive properties. Express Polym. Lett. 5: 385–400.

Wang, W.B., J.P. Zhang, and A.Q. Wang. 2009b. Preparation and swelling properties of superabsorbent nanocomposites based on natural guar gum and organo-vermiculite. Appl. Clay Sci. 46: 21–26.

Wang, W.B., N.H. Zhai, and A.Q. Wang. 2011g. Preparation and swelling characteristics of a superabsorbent nanocomposite based on natural guar gum and cation-modified vermiculite. J. Appl. Polym. Sci. 119: 3675–3686.

Wang, W.B., Y.A. Zheng, and A.Q. Wang. 2008b. Syntheses and properties of the superabsorbent composites based on natural guar gum and attapulgite. Polym. Adv. Technol. 19: 1852–1859.

Wang, X.H. and A.Q. Wang. 2010b. Adsorption characteristics of chitosan-g-poly(acrylic acid)/attapulgite hydrogel composite for Hg(II) ions from aqueous solution. Sep. Sci. Technol. 45: 2086–2094.

Wang, X.H. and A.Q. Wang. 2010c. Removal of Cd(II) from aqueous solution by the composite hydrogel based on attapulgite. Environ. Technol. 31: 745–753.

Wang, X.H. and A.Q. Wang. 2012. Equilibrium isotherm and mechanism studies of Pb(II) and Cd(II) ions onto hydrogel composite based on vermiculite. Des. Water Treat. 48: 38–49.

Wang, X.H., Y.T. Xie, and A.Q. Wang. 2010f. Adsorption behaviors of copper ion(II) on chitosan-g-poly(acrylic acid)/vermiculite composites. China Mining Mag. 19: 101–104.

Wang, X.H., Y.A. Zheng, and A.Q. Wang. 2009c. Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite composites. J. Hazard. Mater. 168: 970–977.

Wang, X.Y., Y.M. Du, J.W. Luo, B.F. Lin, and J. F. Kennedy. 2007. Chitosan/organic rectorite nanocomposite films: Structure, characteristic and drug delivery behavior. Carbohydr. Polym. 69: 41–49.

Wang, X.Y., B. Liu, J.L. Ren, C.F. Liu, X.H. Wang, J. Wu, and R.C. Sun. 2010g. Preparation and characterization of new quaternized carboxymethyl chitosan/rectorite nanocomposite. Composited Sci. Technol. 70: 1161–1167.

Wang, X.Y., S.P. Strand, Y.M. Du, and M. Kjell. 2010h. Chitosan–DNA–rectorite nanocomposites: Effect of chitosan chain length and glycosylation. Carbohydr. Polym. 79: 590–596.

Wang, Y.Z., X.N. Shi, W.B. Wang, and A.Q. Wang. 2013a. Ethanol-assisted dispersion of attapulgite and its effect on improving properties of alginate-based superabsorbent nanocomposite. J. Appl. Polym. Sci. 129: 1080–1088.

Wang, Y.Z., W.B. Wang, X.N. Shi, and A.Q. Wang. 2013b. Enhanced swelling and responsive properties of an alginate-based superabsorbent hydrogel by sodium p-styrenesulfonate and attapulgite nanorods. Polym. Bull. 70: 1181–1193.

Wu, D., B. Zhang, C. Li, Z. Zhang, and H. Kong. 2006. Simultaneous removal of ammonium and phosphate by zeolite synthesized from fly ash as influenced by salt treatment. J. Colloid Interface Sci. 304: 300–306.

Wu, J.H., J.M. Lin, M. Zhou, and C.R. Wei. 2000. Synthesis and properties of starchgraft-polyacrylamide/clay superabsorbent composite. Macromol. Rapid Commun. 21: 1032–1034.

Xie, Y.T. and A.Q. Wang. 2009a. Effects of modified vermiculite on water absorbency and swelling behavior of chitosan-g-poly(acrylic acid)/vermiculite superabsorbent composite. J. Compos. Mater. 43: 2401–2417.

Xie, Y.T. and A.Q. Wang. 2009b. Preparation and properties of chitosan-g-poly(acrylic acid)/ sepiolite superabsorbent composites. Polym. Mater. Sci. Eng. 25: 129–132.

Xie, Y.T. and A.Q. Wang. 2009c. Synthesis, characterization and performance of chitosan-g-poly (acrylic acid)/vermiculite superabsorbent composites. J. Polym. Res. 16: 143–150.

Xie, Y.T. and A.Q. Wang. 2010. Preparation and swelling behaviour of cts-g-poly(acrylic acid)/muscovite superabsorbent composites. Iran. Polym. J. 19: 131–141.

Xie, Y.T., A.Q. Wang, and G. Liu. 2010. Effects of modified sepiolite on water absorbency and swelling behavior of chitosan-g-poly (acrylic acid)/sepiolite superabsorbent composite. Polym. Composit. 31: 89–96.

Xu, J.X., J.P. Zhang, Q. Wang, and A.Q. Wang. 2011. Disaggregation of palygorskite crystal bundles via high-pressure homogenization. Appl. Clay Sci. 54: 118–123.

Xu, R.F., S.J. Xin, X. Zhou, W. Li, F. Cao, X.Y. Feng, and H.B. Deng. 2012. Quaternized chitosan-organic rectorite intercalated composites based nanoparticles for protein controlled release. Int. J. Pharm. 438: 258–265.

Yan, L., Q. Shuai, X. Gong, Q. Gu, and H. Yu. 2009. Metallic iron filters for universal access to safe drinking water. Clean-Soil Air Water 37: 392–397.

Yang, H.X., S.B. Hua, W.B. Wang, and A.Q. Wang. 2011. Composite hydrogel beads based on chitosan and laponite: Preparation, swelling, and drug release behavior. Iran. Polym. J. 20: 479–490.

Yang, H.X., W.B. Wang, and A.Q. Wang. 2012. A pH-sensitive biopolymer-based superabsorbent nanocomposite from sodium alginate and attapulgite: Synthesis, characterization and swelling behaviors. J. Dispersion Sci. Technol. 33: 1154–1162.

Yang, H.X., W.B. Wang, J.P. Zhang, and A.Q. Wang. 2013. Preparation, characterization and drug-release behaviors of a pH-sensitive composite hydrogel bead based on guar gum, attapulgite and sodium alginate. Int. J. Polym. Mater. 62: 369–376.

Yao, S., J. Li, and Z. Shi. 2009. Phosphate ion removal from aqueous solution using an iron oxide-coated fly ash adsorbent. Adsorpt. Sci. Technol. 27: 603–608.

Yuan, L. and T. Kusuda. 2005. Adsorption of ammonium and nitrate ions by poly(N-isopropylacrylamide) gel and poly(N-isopropylacrylamide-co-chlorophyllin) gel in different states. J. Appl. Polym. Sci. 96: 2367–2372.

Zeng, L., X. Li, and J. Liu. 2004. Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. Water Res. 38: 1318–1326.

Zhang, J., K.H. Lee, L. Cui, and T. Jeong. 2009. Formation of organic nanoparticles by freezedrying and their controlled release. J. Ind. Eng. Chem. 15: 185–189.

Zhang, J., W.Q. Wang, Y.P. Wang, J.Y. Zeng, S.T. Zhang, Z.Q. Lei, and X.T. Zhao. 2007c. Preparation and characterization of montmorillonite/carrageen/guar gum gel spherical beads. Polym. Polym. Compos. 15: 131–136.

Zhang, J.P., Y.L. Jin, and A.Q. Wang. 2011. Rapid removal of Pb(II) from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite/sodium humate composite hydrogels. Environ Technol. 32: 523–531.

Zhang, J.P., A. Li, and A.Q. Wang. 2005. Swelling behaviors and application of poly(acrylic acid-co-acrylamide)/sodium humate/attapulgite superabsorbent composite. Polym. Adv. Technol. 16: 813–820.

Zhang, J.P., A. Li, and A.Q. Wang. 2006. Study on superabsorbent composite. VI. Preparation, characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgite superabsorbent composite. Carbohydr. Polym. 65: 150–158.

Zhang, J.P. and A.Q. Wang. 2010. Adsorption of Pb(II) from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite/sodium humate composite hydrogels. J. Chem. Eng. Data 55: 2379–2384.

Zhang, J.P., L. Wang, and A.Q. Wang. 2007a. Preparation and properties of chitosang-poly(acrylic acid)/montmorillonite superabsorbent nanocomposite via in situ intercalative polymerization. Ind. Eng. Chem. Res. 46: 2497–2502.

Zhang, J.P., Q. Wang, and A.Q. Wang. 2007b. Synthesis and characterization of chitosang-poly(acrylic acid)/attapulgite superabsorbent composites. Carbohydr. Polym. 68: 367–374.

Zhang, J.P., Q. Wang, and A.Q. Wang. 2010a. In situ generation of sodium alginate/ hydroxyapatite nanocomposite beads as drug controlled release matrices. Acta Biomater.

6: 445–454.

Zhang, J.P., Q. Wang, X.L. Xie, X. Li, and A.Q. Wang. 2010b. Preparation and swelling properties of pH-sensitive sodium alginate/layered double hydroxides hybrid beads for controlled release of diclofenac sodium. J. Biomed. Mater. Res. B 92B: 205–214.

Zheng, Y.A., S.B. Hua, and A.Q. Wang. 2010. Adsorption behavior of Cu 2+ from aqueous solutions onto starch-g-poly(acrylic acid)/sodium humate hydrogels. Desalination 263: 170–175.

Zheng, Y.A., P. Li, and J.P. Zhang. 2007. Synthesis, characterization and swelling behaviors of poly(sodium acrylate)/vermiculite superabsorbent composites. Eur. Polym. J. 43: 1691–1698.

Zheng, Y.A. and A.Q. Wang. 2009. Evaluation of ammonium removal using a chitosan-g-poly (acrylic acid)/rectorite hydrogel composite. J. Hazard. Mater. 171: 671–677.

Zheng, Y.A. and A.Q. Wang. 2010a. Nitrate adsorption using poly(dimethyl diallyl ammonium chloride)/polyacrylamide hydrogel. J. Chem. Eng. Data. 55: 3494–3500.

Zheng, Y.A. and A.Q. Wang. 2010b. Potential of phosphate removal using Al 3+ -crosslinking chitosan-g-poly(acrylic acid)/vermiculite ionic hybrid. Adsorpt. Sci. Technol. 28: 89–99.

Zheng, Y.A. and A.Q. Wang. 2010c. Enhanced adsorption of ammonium using hydrogel composites based on chitosan and halloysite. J. Macromol. Sci. Part A Pure Appl. Chem. 47: 33–38.

Zheng, Y.A. and A.Q. Wang. 2012. Granular hydrogel initiated by Fenton reagent and their performance on Cu(II) and Ni(II) removal. Chem. Eng. J. 200: 601–610.

Zheng, Y.A., Y.T. Xie, and A.Q. Wang. 2009a. Adsorption of Pb 2+ onto chitosan-grafted-poly (acrylic acid)/sepiolite composite. Environ. Sci. 30: 2575–2579.

Zheng, Y.A., Y.T. Xie, and A.Q. Wang. 2012. Rapid and wide pH-independent ammoniumnitrogen removal using a composite hydrogel with three-dimensional networks. Chem. Eng. J. 179: 90–98.

Zheng, Y.A., J.P. Zhang, and A.Q. Wang. 2009b. Fast removal

of ammonium-nitrogen from aqueous solution using
chitosan-g-poly (acrylic acid)/attapulgite composite. Chem.
Eng. J. 155: 215-222.

5 Chapter 5: Iron Oxide Magnetic Composite Adsorbents for Heavy Metal Pollutant Removal

Al-Assaf, S., M. Sakata, C. McKenna, E.H. Aoki, and G.O. Phillips. 2009. Molecular associations in acacia gums. Struct. Chem. 20: 325–336.

Ali, I. 2012. New generation adsorbents for water treatment. Chem. Rev. 112: 5073–5091.

Ambashta, R.D. and M. Sillanpää. 2010. Water purification using magnetic assistance: A review. J. Hazard. Mater. 180: 38–49.

Babel, S. and T.A. Kurniawan. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. J. Hazard. Mater. B97: 219–240.

Badruddoza, A.Z.M., A.S.H. Tay, P.Y. Tan, K. Hidajat, and M.S. Uddin. 2011. Carboxymethylβ-cyclodextrin conjugated magnetic nanoparticles as nano-adsorbents for removal of copper ions: Synthesis and adsorption studies. J. Hazard. Mater. 185: 1177–1186.

Banerjee, S.S. and D.-H. Chen. 2007. Fast removal of copper ions by gum arabic modified magnetic nano-adsorbent. J. Hazard. Mater. 147: 792–799.

Barakat, M.A. 2011. New trends in removing heavy metals from industrial wastewater: A review. Arab. J. Chem. 4: 361–377.

Bée, A., D. Talbot, S. Abramson, and V. Dupuis. 2011. Magnetic alginate beads for Pb(II) ions removal from wastewater. J. Colloid Interface Sci. 362: 486–492.

Bicak, O., Z. Ekmekci, D.J. Bradshaw, and P.J. Harris. 2007. Adsorption of guar gum and CMC on pyrite. Miner. Eng. 20: 996–1002.

Chen, Y. and J. Wang. 2012. The characteristics and mechanism of Co(II) removal from aqueous solution by a novel xanthate-modified magnetic chitosan. Nucl. Eng. Des. 242: 452–457.

Crini, G. 2005. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog. Polym. Sci. 30: 38–70.

Demirbas, A. 2008. Heavy metal adsorption onto agro-based waste materials: A review. J. Hazard. Mater. 157: 220–229.

Deng, J.-H., X.-R. Zhang, G.-M. Zeng, J.-L. Gong, Q.-Y. Niu, and J. Liang. 2013. Simultaneous removal of Cd(II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. Chem. Eng. J. 226: 189–200.

Denizli, A., G. Ozkan, and M.Y. Arica. 2000. Preparation and characterization of magnetic polymethylmethacrylate microbeads carrying ethylenediamine for removal of Cu(II), Cd(II), Pb(II), and Hg(II) from aqueous solutions. J. Appl. Polym. Sci. 78: 81–89.

Denkbas, E.B., E. Kilicay, C. Birlikseven, and E. Oztürk. 2002. Magnetic chitosan microspheres: Preparation and characterization. React. Funct. Polym. 50: 225–232.

Dias, A.M.G.C., A. Hussain, A.S. Marcos, and A.C.A. Roque. 2011. A biotechnological perspective on the application of iron oxide magnetic colloids modified with polysaccharides. Biotechnol. Adv. 29: 142–155.

Dodi, G., D. Hritcu, G. Lisa, and M.I. Popa. 2012. Core–shell magnetic chitosan particles functionalized by grafting: Synthesis and characterization. Chem. Eng. J. 203: 130–141.

Dung, T., T. Danh, L. Ho, D. Chien, and N. Due. 2009. Structural and magnetic properties of starch coated magnetic nanoparticles. J. Exp. Nanosci. 4: 259–267.

Faraudo, J., J.S. Andreu, and J. Camacho. 2013. Understanding diluted dispersions of superparamagnetic particles under strong magnetic fields: A review of concepts, theory and simulations. Soft Matter 9: 6654–6664. doi: 10.1039/c3sm00132f.

Farooq, U., J.A. Kozinski, M.A. Khan, and M. Athar. 2010. Biosorption of heavy metal ions using wheat based biosorbents—A review of the recent literature. Bioresour. Technol. 101: 5043–5053.

Feng, L., M. Cao, X. Ma, Y. Zhu, and C. Hu. 2012. Superparamagnetic high-surface-area Fe_3O_4 nanoparticles as adsorbents for arsenic removal. J. Hazard. Mater. 217–218: 439–446.

Fu, F. and Q. Wang. 2011. Removal of heavy metal ions from wastewaters: A review. J. Environ. Manag. 92: 407–418.

Fungaro, D.A., M. Yamaura, and G.R. Craesmeyer. 2012. Uranium removal from aqueous solution by zeolite from fly ash-iron oxide magnetic nanocomposite. Int. Rev. Chem. Eng. (I.RE.CH.E.) 4: 353–358.

Gao, F., Y. Cai, J. Zhou, X. Xie, W. Ouyang, and Y. Zhang. 2010. Pullulan acetate coated magnetite nanoparticles for hyper-thermia: Preparation, characterization and in vitro experiments. Nano Res. 3: 23–31.

Giakisikli, G. and A.N. Anthemidis. 2013. Magnetic materials as sorbents for metal/metalloid preconcentration and/or separation. A review. Anal. Chim. Acta 789: 1–16.

Gong, J.L., X.Y. Wang, G.M. Zeng, L. Chen, J.H. Deng, X.R. Zhang, and Q.Y. Niu. 2012. Copper (II) removal by pectin-iron oxide magnetic nanocomposite adsorbent. Chem. Eng. J. 185–186: 100–107.

Guibal, E. 2004. Interactions of metal ions with chitosan-based sorbents: A review. Sep. Purif. Technol. 38: 43–74.

Gupta, V.K. and A. Nayak. 2012. Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe_2O_3 nanoparticles. Chem. Eng. J. 180: 81–90.

Horak, D., E. Petrovsky, and A. Kapicka. 2007. Synthesis and characterization of magnetic poly(glycidyl methacrylate) microspheres. J. Magn. Magn. Mater. 311: 500–506.

Hritcu, D., G. Dodi, D. Humelnicu, and M.I. Popa. 2012a. Magnetic chitosan composite particles: Evaluation of thorium and uranyl ion adsorption from aqueous solutions. Carbohydr. Polym. 87: 1185–1191.

Hritcu, D., G. Dodi, and M.I. Popa. 2012b. Heavy metal ion adsorption on chitosan-magnetite microspheres. Int. Rev. Chem. Eng. 4: 364–368.

Hritcu, D., G. Dodi, M. Silion, N. Popa, and M.I. Popa. 2011. Composite magnetite-chitosan microspheres: In-situ preparation and characterization. Polym. Bull. 67: 177–186.

Hu, J., I.M.C. Lo, and G. Chen. 2007. Comparative study of various magnetic nanoparticles for Cr(VI) removal. Sep.

Purif. Technol. 56: 249–256.

Hu, J., D. Shao, C. Chen, G. Sheng, J. Li, X. Wang, and M. Nagatsu. 2010. Plasma-induced grafting of cyclodextrin onto multiwall carbon nanotube/iron oxides for adsorbent application. J. Phys. Chem. B 114: 6779–6785.

Hu, M., S. Zhang, B. Pan, W. Zhang, L. Lv, and Q. Zhang. 2012. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. J. Hazard. Mater. 211–212: 317–331.

Hu, Y., Y. Bo, L. Yaobo, and C. Rong Shi. 2009. Preparation of magnetic chitosan microspheres and its applications in wastewater treatment. Sci. China Ser. B: Chem. 52: 249–256.

IARC. 1990. Monograph on the evaluation of carcinogenic risk to humans. Chromium, nickel and welding. Int. Agency Res. Cancer. 49: 187–208.

Jin, Y., F. Liu, M. Tong, Y. Hou, and Y. Jin. 2012. Removal of arsenate by cetyltrimethylammonium bromide modified magnetic nanoparticles. J. Hazard. Mater. 227–228: 461–468.

Lee, J., T. Isobe, and M. Senna. 1996. Preparation of ultrafine Fe_3O_4 particles by precipitation in the presence of PVA at high pH. J. Colloid Interface Sci. 177: 490–494.

Li, B., D. Jia, Y. Zhou, Q. Hu, and W. Cai. 2006. In situ hybridization to chitosan/magnetite nanocomposite induced by the magnetic field. J. Magn. Magn. Mater. 306: 223–227.

Li, G., Y. Jiang, K. Huang, P. Ding, and J. Chen. 2008. Preparation and properties of magnetic Fe_3O_4-chitosan nanoparticles. J. Alloys Compd. 466: 451–456.

Li, J., Z. Guo, S. Zhang, and X. Wang. 2011. Enrich and seal radionuclides in magnetic agarose microspheres. Chem. Eng. J. 172: 892–897.

Li, X.S., G.T. Zhu, Y.B. Luo, B.F. Yuan, and Y.Q. Feng. 2013. Synthesis and applications of functionalized magnetic materials in sample preparation. Trends Anal. Chem. 45: 233–247.

Liu, X.W., Q.Y. Hu, Z. Fang, X.J. Zhang, and B.B. Zhang. 2009. Magnetic chitosan nanocomposites: A useful recyclable took for heavy metal ion removal. Langmuir 25: 3–8.

Ma, H., X. Qi, Y. Maitani, and T. Nagai. 2007. Preparation and characterization of superparamagnetic iron oxide nanoparticles stabilized by alginate. Int. J. Pharm. 333: 177–186.

Manahan, S.E. 2001. Fundamentals of Environmental Chemistry. Boca Raton, FL: CRC Press LLC.

Monier, M., D.M. Ayad, Y. Wei, and A.A. Sarhan. 2010. Adsorption of Cu(II), Co(II) and Ni(II) ions by modified chitosan chelating resin. J. Hazard. Mater. 177: 962–970.

Mornet, S., J. Portier, and E. Duguet. 2005. A method for synthesis and functionalization of ultra small superparamagnetic covalent carriers based on maghemite and dextran. J. Magn. Magn. Mater. 293: 127–134.

Mourya, V.K. and N.N. Inamdar. 2008. Chitosan-modifications and applications: Opportunities galore. React. Funct. Polym. 68: 1013–1051.

Murbe, J., A. Rechtenbach, and J. Topfer. 2008. Synthesis and physical characterization of magnetite nanoparticles for biomedical applications. Mater. Chem. Phys. 110: 426–433.

Ngomsik, A.F., A. Bee, J.M. Siaugue, D. Talbot, V. Cabuila, and G. Cote. 2009. Co(II) removal by magnetic alginate beads containing Cyanex 272 ® . J. Hazard. Mater. 166: 1043–1049.

Nordberg, G., B. Fowler, M. Nordberg, and L.F. Friberg. 2007. Handbook on the Toxicity of Metals, 3rd edn., pp. 743–758. Amsterdam, the Netherlands: Elsevier.

O'Connell, D.W., C. Birkinshaw, and T.F. O'Dwyer. 2008. Heavy metal adsorbents prepared from the modification of cellulose: A review. Bioresour. Technol. 99: 6709–6724.

Panchev, I.N., A. Slavov, Kr. Nikolova, and D. Kovacheva. 2010. On the water-sorption properties of pectin. Food Hydrocolloids 24: 763–769.

Panneerselvam, P., N. Morad, and K.A. Tan. 2011. Magnetic nanoparticle (Fe_3O_4) impregnated onto tea waste for the removal of nickel(II) from aqueous solution. J. Hazard. Mater. 186: 160–168.

Parham, H., B. Zargar, and R. Shiralipour. 2012. Fast and efficient removal of mercury from water samples using magnetic iron oxide nanoparticles modified with 2-mercaptobenzothiazole. J. Hazard. Mater. 205–206: 94–100.

Petrova, T.M., L. Fachikov, and J. Hristov. 2011. The magnetite as adsorbent for some hazardous species from aqueous solutions: A review. Int. Rev. Chem. Eng. 3: 134–152.

Petrova, T.M., V.A. Karadjova, L. Fachikov, and J. Hristov. 2012. Silver recovery from spent photographic solutions by natural magnetite: Attempts to estimate the process mechanism and optimal process conditions. Int. Rev. Chem. Eng. 4: 373–378.

Podzus, P.E., M.E. Daraio, and S.E. Jacobo. 2009. Chitosan magnetic microspheres for technological applications: Preparation and characterization. Physica B. 404: 2710–2712.

Safarik I., K. Horska, K. Pospiskova, and M. Safarikova. 2012. Magnetically responsive activated carbons for bio- and environmental applications. Int. Rev. Chem. Eng. 4: 346–352.

Safdarian, M., P. Hashemi, and M. Adeli. 2013. One-step synthesis of agarose coated magnetic nanoparticles and their application in the solid phase extraction of Pd(II) using a new magnetic field agitation device. Anal. Chim. Acta 774: 44–50.

Saravanan, P., V.T.P. Vinod, B. Sreedhar, and R.B. Sashidhar. 2012. Gum kondagogu modified magnetic nano-adsorbent: An efficient protocol for removal of various toxic metal ions. Mater. Sci. Eng. C 32: 581–586.

Shena, H., S. Pana, Y. Zhanga, X. Huang, and H. Gong. 2012. A new insight on the adsorption mechanism of amino-functionalized nano-Fe_3O_4 magnetic polymers in Cu(II), Cr(VI) co-existing water system. Chem. Eng. J. 183: 180–191.

Simeonidis, K., Th. Gkinis, S. Tresintsi, C. Martinez-Boubeta, G. Vourlias, I. Tsiaoussis, G. Stavropoulos, M. Mitrakas, and M. Angelakeris. 2011. Magnetic separation of hematitecoated Fe_3O_4 particles used as arsenic adsorbents. Chem. Eng. J. 168: 1008–1015.

Song, K., W. Kim, C.Y. Suh, D. Shin, K.S. Ko, and K. Ha. 2013. Magnetic iron oxide nanoparticles prepared by electrical wire explosion for arsenic removal. Powder

Technol. 246: 572–574.

Sun, X., L. Yang, H. Xing, J. Zhao, X. Li, Y. Huang, and H. Liu. 2013. Synthesis of polyethylenimine-functionalized poly(glycidyl methacrylate) magnetic microspheres and their excellent Cr(VI) ion removal properties. Chem. Eng. J. 234: 338–345.

Tang, S.C.N. and I.M.C. Lo. 2013. Magnetic nanoparticles: Essential factors for sustainable environmental applications. Water Res. 47: 2613–2632.

Thompson, J. and J. Bannigan. 2008. Cadmium: Toxic effects on the reproductive system and the embryo. Reprod. Toxicol. 25(3): 304–315.

Tran, H.V., L.D. Tran, and T.N. Nguyen. 2010. Preparation of chitosan/magnetite composite beads and their application for removal of Pb(II) and Ni(II) from aqueous solution. Mater. Sci. Eng. C 30: 304–310.

Tripathi, A., J.S. Melo, and S.F. D'Souza. 2013. Uranium (VI) recovery from aqueous medium using novel floating macroporous alginate-agarose-magnetite cryobeads. J. Hazard. Mater. 246–247: 87–95.

Varma, A.J., S.V. Deshpande, and J.F. Kennedy. 2004. Metal complexation by chitosan and its derivatives: A review. Carbohydr. Polym. 55: 77–93.

Vinod, V.T.P. and R.B. Sashidhar. 2009. Solution and conformational properties of gum kondagogu (Cochlospermum gossypium)—A natural product with immense potential as a food additive. Food Chem. 116: 686–692.

Wang, L., C. Tian, G. Mu, L. Sun, H. Zhang, and H. Fu. 2012. Magnetic nanoparticles/ graphitic carbon nanostructures composites: Excellent magnetic separable adsorbents for precious metals from aqueous solutions. Mater. Res. Bull. 47: 646–654.

Wang, X. and M.L. Brusseau. 1995. Simultaneous complexation of organic compounds and heavy metals by a modified cyclodextrin. Environ. Sci. Technol. 29: 2632–2635.

Wang, X., C. Zhao, P. Zhao, P. Dou, Y. Ding, and P. Xu. 2009. Gellan gel beads containing magnetic nanoparticles: An effective biosorbent for the removal of heavy metals from aqueous system. Bioresour. Technol. 100: 2301–2304.

Wan Ngah, W.S., L.C. Teong, and M.A.K.M. Hanafiah. 2011. Adsorption of dyes and heavy metal ions by chitosan composites: A review. Carbohydr. Polym. 83: 1446–1456.

Zhao, X., L. Lv, B. Pana, W. Zhang, S. Zhang, and Q. Zhang. 2011. Polymer-supported nanocomposites for environmental application: A review. Chem. Eng. J. 170: 381–394.

Zhao, Y.G., H.Y. Shen, S.D. Pan, and M.Q. Hu. 2010. Synthesis, characterization and properties of ethylenediamine-functionalized Fe_3O_4 magnetic polymers for removal of Cr(VI) in wastewater. J. Hazard. Mater. 182: 295–302.

Zhou, L., Y. Wang, Z. Liu, and Q. Huang. 2009. Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres. J. Hazard. Mater. 161: 995–1002.

Zhu J., S. Wei, M. Chen, H. Gu, S.B. Rapole, S. Pallavkar, T.C. Ho, J. Hopper, and Z. Guo. 2013. Magnetic nanocomposites for environmental remediation. Adv. Powder Technol. 24: 459–467.

6 Chapter 6: Biopolymer-Zeolite Composites as Biosorbents for Separation Processes

Agarwal, S., S. Sundarrajan, and S. Ramakrishna. 2012. Functionalized cellulose: PET polymer fibers with zeolites for detoxification against nerve agents. J. Inorg. Mater. 27: 332–336.

Akkaya, R. and U. Ulusoy. 2008. Adsorptive features of chitosan entrapped in polyacrylamide hydrgel for Pb^{2+}, UO_2^{2+}, and Th^{4+}. J. Hazard. Mater. 151: 380–388.

Armagan, B., M. Turan, and M.S. Celik. 2004. Equilibrium studies on the adsorption of reactive azo dyes into zeolite. Desalination 170: 33–39.

Aytas, S.O., S. Akyil, and M. Eral. 2004. Adsorption and thermodynamic behavior of uranium on natural zeolite. J. Radioanal. Nucl. Chem. 260: 119–125.

Bastani, D., N. Esmaeili, and M. Asadollahi. 2013. Polymeric mixed matrix membranes containing zeolites as ller for gas separation applications: A review. J. Ind. Eng. Chem. 19: 375–393.

Bedelean, H., M. Stanca, A. Măicăneanu, and S. Burca. 2006. Zeolitic volcanic tuffs from Măcicaş (Cluj County), natural raw materials used for NH_4^+ removal from wastewaters, Geologia 52: 43–49.

Bhat, S.D. and T.M. Aminabhavi. 2007a. Zeolite K-LTL-loaded sodium alginate mixed matrix membranes for pervaporation dehydration of aqueous-organic mixtures. J. Membr. Sci. 306: 173–185.

Bhat, S.D. and T.M. Aminabhavi. 2007b. Pervaporation separation using sodium alginate and its modified membranes—A review. Sep. Purif. Rev. 36: 203–229.

Bhat, S.D. and T.M. Aminabhavi. 2009. Pervaporation-aided dehydration and esterification of acetic acid with ethanol using 4A zeolite-filled cross-linked sodium alginate-mixed matrix membranes. J. Appl. Polym. Sci. 113: 157–168.

Bondarev, A., S. Mihai, O. Pantea, and S. Neagoe. 2011. Use of biopolymers for the removal of metal ion contaminants from water. Macromol. Symp. 303: 78–84.

Caro, J., M. Noack, P. Kölsch, and R. Schäfer. 2000.

Zeolite membranes—State of their development and perspective. Microporous Mesoporous Mater. 38: 3–24.

Chao, H.P. and S.H. Chen. 2012. Adsorption characteristics of both cationic and oxyanionic metal ions on hexadecyltrimethylammonium bromide-modi�ed NaY zeolite. Chem. Eng. J. 193–194: 283–289.

Chen, D., W. Li, Y. Wub, Q. Zhu, Z. Lu, and G. Du. 2013. Preparation and characterization of chitosan-montmorillonite magnetic microspheres and its application for the removal of Cr (VI). Chem. Eng. J. 221: 8–15.

Chen, Z., M. Deng, Y. Chen, G. He, M. Wu, and J. Wang. 2004. Preparation and performance of cellulose acetate-polyethyleneimine blend micro�ltration membranes and their applications. J. Membr. Sci. 235: 73–86.

Chmielewská, E., L. Sabová, H. Peterlik, and A. Wu. 2011. Batch-wise adsorption, SAXS and microscopic studies of zeolite pelletized with biopolymeric alginate. Braz. J. Chem. Eng. 28: 63–71.

Choi, J.W., K.S. Yang, D.J. Kim, and C.E. Lee. 2009. Adsorption of zinc and toluene by alginate complex impregnated with zeolite and activated carbon. Curr. Appl. Phys. 9: 694–697.

Crini, G. 2005. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog. Polym. Sci. 30: 38–70.

Dinu, M.V. and E.S. Dragan. 2008. Heavy metals adsorption on some iminodiacetate chelating resins as a function of the adsorption parameters. React. Funct. Polym. 68: 1346–1354.

Dinu, M.V. and E.S. Dragan. 2010a. Adsorption of heavy metals on ionic composites based on chitosan. Bull. Inst. Pol. Iasi. Tom LVI(LX): 171–178.

Dinu, M.V. and E.S. Dragan. 2010b. Evaluation of Cu 2+ , Co 2+ and Ni 2+ ions removal from aqueous solution using a novel chitosan-clinoptilolite composite: Kinetics and isotherms. Chem. Eng. J. 160: 157–163.

Dinu, M.V., E.S. Dragan, and A.W. Trochimczuk. 2009. Sorption of Pb(II), Cd(II) and Zn(II) by iminodiacetate chelating resins in non-competitive and competitive conditions. Desalination 249: 374–379.

Dogan, H. 2012. Preparation and characterization of calcium alginate-based composite adsorbents for the removal of Cd, Hg, and Pb ions from aqueous solution. Toxicol. Environ. Chem. 94: 482–499.

Dogan, H. and N.D. Hilmioglu. 2010a. Zeolite-filled regenerated cellulose membranes for pervaporative dehydration of glycerol. Vacuum 84: 1123–1132.

Dogan, H. and N.D. Hilmioglu. 2010b. Chitosan coated zeolite filled regenerated cellulose membrane for dehydration of ethylene glycol-water mixtures by pervaporation. Desalination 258: 120–127.

Dragan, E.S. and M.V. Dinu. 2009. Removal of copper ions from aqueous solution by adsorption on ionic hybrids based on chitosan and clinoptilolite. Ion Exchange Lett. 2: 15–18.

Dragan, E.S., M.V. Dinu, and M. Mihai. 2011. Chapter 6: Separations by multicomponent ionic systems based on natural and synthetic polycations. In Sengupta, A.K. (ed.), Ion Exchange and Solvent Extraction: A Series of Advances, pp. 233–291. CRC Press, Boca Raton, FL.

Dragan, E.S., M.V. Dinu, and D. Timpu. 2010. Preparation and characterization of novel composites based on chitosan and clinoptilolite with enhanced adsorption properties for Cu^{2+}. Bioresour. Technol. 101: 812–817.

Fu, F. and Q. Wang. 2011. Removal of heavy metal ions from wastewaters: A review. J. Environ. Manag. 92: 407–418.

Furlan, F.R., L.G. De Melo da Silva, A.F. Morgado, A.A.U. de Souza, and S.M.A.G. Ulson de Souza. 2010. Removal of reactive dyes from aqueous solutions using combined coagulation–flocculation and adsorption on activated carbon. Resour. Conserv. Recycl. 54: 283–290.

Günay, A., E. Arslankaya, and I. Tosun. 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. J. Hazard. Mater. 146: 362–371.

Han, R., W. Zou, Y. Wang, and L. Zhu. 2007. Removal of U(VI) from aqueous solutions by manganese oxide coated zeolite: Discussion of adsorption isotherms and pH effect. J. Environ. Radioact. 93: 127–143.

Hasan, S., T.K. Ghosh, M.A. Prelas, D.S. Viswanath, and V.M. Boddu. 2007. Adsorption of uranium on a novel bioadsorbent-chitosan-coated perlite. Nucl. Technol. 159: 59–71.

Hernández-Montoya, V., M.A. Pérez-Cruz, D.I. Mendoza-Castillo, M.R. Moreno-Virgen, and A. Bonilla-Petriciolet. 2013. Competitive adsorption of dyes and heavy metals on zeolitic structures. J. Environ. Manag. 116: 213–221.

Hritcu, D., D. Humelnicu, G. Dodi, and M.I. Popa. 2012. Magnetic chitosan composite particles: Evaluation of thorium and uranyl ion adsorption from aqueous solutions. Carbohydr. Polym. 87: 1185–1191.

Humelnicu, D., M.V. Dinu, and E.S. Dragan. 2011. Adsorption characteristics of UO_2^{2+} and Th^{4+} ions from simulated radioactive solutions onto chitosan-clinoptilolite sorbents. J. Hazard. Mater. 185: 447–455.

Ibanez, J.P. and Y. Umetsu. 2002. Potential of protonated alginate beads for heavy metals uptake. Hydrometallurgy 64: 89–99.

Idris, A., N. Suriani, M. Ismail, N. Hassan, E. Misran, and A.F. Ngomsik. 2012. Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb(II) removal in aqueous solution. J. Ind. Eng. Chem. 18: 1582–1589.

Ji, F., C. Li, B. Tang, J. Xu, G. Lu, and P. Liu. 2012. Preparation of cellulose acetate-zeolite composite fiber and its adsorption behavior for heavy metal ions in aqueous solution. Chem. Eng. J. 209: 325–333.

Ji, F., C. Li, J. Xu, and P. Liu. 2013. Dynamic adsorption of Cu(II) from aqueous solution by zeolite-cellulose acetate blend fiber in fixed-bed. Colloids Surf. A: Physicochem. Eng. Asp. 434: 88–94.

Kahya, S., O. Şanlıb, and E. Çamurlu. 2011. Crosslinked sodium alginate and sodium alginate-clinoptilolite (natural zeolite) composite membranes for pervaporation separation of dimethylformamide-water mixtures: A comparative study. Des. Water Treat. 25: 297–309.

Kariduraganavar, M.Y., A.A. Kittur, S.S. Kittur, S.S. Kulkarni, and K. Ramesh. 2004. Development of novel pervaporation membranes for the separation of water-isopropanol mixtures using sodium alginate and NaY zeolite. J. Membr. Sci. 238: 165–175.

Kilincarslan, A. and S. Akyil. 2005. Uranium adsorption characteristic and thermodynamic behavior of clinoptilolite zeolite. J. Radioanal. Nucl. Chem. 264: 541–548.

Kittur, A.A., S.S. Kulkarni, M.I. Aralaguppi, and M.Y. Kariduraganavar. 2005. Preparation and characterization of novel pervaporation membranes for the separation of water-isopropanol mixtures using chitosan and NaY zeolite. J. Membr. Sci. 247: 75–86.

Kittur, A.A., S.M. Tambe, S.S. Kulkarni, and M.Y. Kariduraganavar. 2004. Pervaporation separation of water–acetic acid mixtures through NaY zeolite-incorporated sodium alginate membranes. J. Appl. Polym. Sci. 94: 2101–2109.

Li, S.G., V.A. Tuan, R.D. Noble, and J.L. Falconer. 2001. Pervaporation of water-THF mixtures using zeolite membranes. Ind. Eng. Chem. Res. 40: 4577–4585.

Libby, B., W.H. Smyrl, and E.L. Cussler. 2003. Polymer–zeolite composite membranes for direct methanol fuel cells. AIChE J. 49: 991–1001.

Lin, J. and Y. Zhan. 2012. Adsorption of humic acid from aqueous solution onto unmodified and surfactant-modified chitosan/zeolite composites. Chem. Eng. J. 200–202: 202–213.

Liu, C. and R. Bai. 2006. Adsorptive removal of copper ions with highly porous chitosancellulose acetate blend hollow fiber membranes. J. Membr. Sci. 284: 313–322.

Liu, L., Y. Wan, Y. Xie, R. Zhai, B. Zhang, and J. Liu. 2012. The removal of dye from aqueous solution using alginate-halloysite nanotube beads. Chem. Eng. J. 187: 210–216.

Ma, X., C. Hu, R. Guo, X. Fang, H. Wu, and Z. Jiang. 2008. HZSM5-filled cellulose acetate membranes for pervaporation separation of methanol-MTBE mixtures. Sep. Purif. Technol. 59: 34–42.

Mahmoodi, N.M. 2013. Magnetic ferrite nanoparticle–alginate composite: Synthesis, characterization and binary system dye removal. J. Taiwan Inst. Chem. Eng. 44: 322–330.

Metin, A.U., H. Çiftçi, and E. Alver. 2013. Efficient removal of acidic dye using low-cost biocomposite beads. Ind. Eng. Chem. Res. 52: 10569–10581.

Mintova, S. and V. Valtchev. 1996. Deposition of zeolite A on vegetal fibers. Zeolites 16: 31–34.

Mintova, S., V. Valtchev, B. Schoeman, and J. Sterte. 1996. Preparation of zeolite Y-vegetal fiber composite materials. J. Porous Mater. 3: 143–150.

Nataraj, S.K., S. Roy, M.B. Patil, M.N. Nadagouda, W.E. Rudzinski, and T.M. Aminabhavi. 2011. Cellulose acetate-coated α-alumina ceramic composite tubular membranes for wastewater treatment. Desalination 281: 348–353.

Nawawi, M., M. Ghazali, and R.Y.M. Huang. 1997. Pervaporation dehydration of isopropanol with chitosan membranes. J. Membr. Sci. 124: 53–62.

Nešić, A.R., S.J. Veličković, and D.G. Antonović. 2012. Characterization of chitosan- montmorillonite membranes as adsorbents for Bezactiv Orange V-3R dye. J. Hazard. Mater. 209–210: 256–263.

Nešić, A.R., S.J. Veličković, and D.G. Antonović. 2013. Modification of chitosan by zeolite A and adsorption of Bezactive Orange 16 from aqueous solution. Composites Part B: Eng. 53: 145–151.

Nibou, D., S. Khemaissia, S. Amokrane, M. Barkat, S. Chegrouche, and A. Mellah. 2011. Removal of UO_2^{2+} onto synthetic NaA zeolite. Characterization, equilibrium and kinetic studies. Chem. Eng. J. 172: 296–305.

Nigiz, F.U., H. Dogan, and N.D. Hilmioglu. 2012. Pervaporation of ethanol-water mixtures using clinoptilolite and 4A filled sodium alginate membranes. Desalination 300: 24–31.

O’Connell, D.W., C. Birkinshaw, and T.F. O’Dwyer. 2008. Heavy metal adsorbents prepared from the modification of cellulose: A review. Bioresour. Technol. 99: 6709–6724.

Pandey, A.K., S.D. Pandey, V. Misra, and S. Devi. 2003. Role of humic acid entrapped calcium alginate beads in removal of heavy metals. J. Hazard. Mater. 98: 177–181.

Park, H.G., T.W. Kim, M.Y. Chae, and I.K. Yoo. 2007. Activated carbon-containing alginate adsorbent for the simultaneous removal of heavy metals and toxic organics. Process Biochem. 42: 1371–1377.

Patil, M.B. and T.M. Aminabhavi. 2008. Pervaporation separation of toluene-alcohol mixtures using silicalite zeolite embedded chitosan mixed matrix membranes. Sep. Purif. Technol. 62: 128–136.

Qiu, M., C. Qian, J. Xu, J. Wu, and G. Wang. 2009. Studies on the adsorption of dyes into clinoptilolite. Desalination 243: 286–292.

Qu, R., C. Sun, F. Ma, Y. Zhang, C. Ji, Q. Xu, C. Wang, and H. Chen. 2009. Removal and recovery of Hg(II) from aqueous solution using chitosan-coated cotton fibers. J. Hazard. Mater. 167: 717–727.

Sanghi, R. and P. Verma. 2013. Decolorisation of aqueous dye solutions by low-cost adsorbents: A review. Color Technol. 129: 85–108.

Saraswathi, M. and B. Viswanath 2012. Separation of water–isopropyl alcohol mixtures with novel hybrid composite membranes. J. Appl. Polym. Sci. 126: 1867–1875.

Spiridon, O.B., E. Preda, A. Botez, and L. Pitulice. 2013. Phenol removal from wastewater by adsorption on zeolitic composite. Environ. Sci. Pollut. Res. 20: 6367–6381.

Sprynskyy, M., B. Buszewski, A.P. Terzyk, and J. Namiesnik. 2006. Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite. J. Colloid Interface Sci. 304: 21–28.

Sun, H., L. Lu, X. Chen, and Z. Jiang. 2008. Surface modified zeolite chitosan membranes for pervaporation dehydration of ethanol. Appl. Surf. Sci. 254: 5367–5374.

Sun, X., B. Peng, Y. Ji, J. Chen, and D. Li. 2009. Chitosan(chitin)-cellulose composite biosorbents prepared using ionic liquid for heavy metal ions adsorption, AIChE J. 55: 2062–2069.

Urtiaga, A., E.D. Gorri, C. Casado, and I. Ortiz. 2003. Pervaporative dehydration of industrial solvents using a zeolite NaA commercial membrane. Sep. Purif. Technol. 32: 207–213.

Vu, D., M. Marquez, and G. Larsen. 2002. A facile method to deposit zeolites Y and L onto cellulose fibers. Microporous Mesoporous Mater. 55: 93–101.

Wang, S. and Y. Peng. 2010. Natural zeolites as effective adsorbents in water and wastewater treatment. Chem. Eng. J. 156: 11–24.

Wang, X., Y. Zheng, and A. Wang. 2009. Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)-attapulgite composites. J. Hazard. Mater. 168: 970–977.

Wang, X.P. 2000. Modified alginate composite membranes for the dehydration of acetic acid. J. Membr. Sci. 170: 71–79.

Wang, Y., Z. Jiang, H. Li, and D. Yang. 2010. Chitosan membranes filled by GPTMS-modified zeolite beta particles with low methanol permeability for DMFC. Chem. Eng. Proc.: Proc. Intensif. 49: 278–285.

Wan Ngah, W.S., N.F.M. Ariff, and M.A.K.M. Hanafiah. 2010. Preparation, characterization, and environmental application of crosslinked chitosan-coated bentonite for tartrazine adsorption from aqueous solutions. Water Air Soil Pollut. 206: 225–236.

Wan Ngah, W.S., L.C. Teong, and M.A.K.M. Hanafiah. 2011. Adsorption of dyes and heavy metal ions by chitosan composites: A review. Carbohydr. Polym. 83: 1446–1456.

Wan Ngah, W.S., L.C. Teong, R.H. Toh, and M.A.K.M. Hanafiah. 2012b. Utilization of chitosan-zeolite composite in the removal of Cu(II) from aqueous solution: Adsorption, desorption and fixed bed column studies. Chem. Eng. J. 209: 46–53.

Wan Ngah, W.S., L.C. Teong, R.H. Toh, and M.A.K.M. Hanafiah. 2013. Comparative study on adsorption and desorption of Cu(II) ions by three types of chitosan-zeolite composites. Chem. Eng. J. 223: 231–238.

Wan Ngah, W.S., L.C. Teong, C.S. Wong, and M.A.K.M. Hanafiah. 2012a. Preparation and characterization of chitosan-zeolite composites. J. Appl. Polym. Sci. 125: 2417–2425.

Xie, J., C. Li, L. Chi, and D. Wu. 2013. Chitosan modified zeolite as a versatile adsorbent for the removal of different pollutants from water. Fuel 103: 480–485.

Yang, G., L. Zhang, T. Peng, and W. Zhong. 2000. Effects of Ca^{2+} bridge cross-linking on structure and pervaporation of cellulose/alginate blend membranes. J. Membr. Sci. 175: 53–60.

Yang, L., X. Ma, and N. Guo. 2012. Sodium alginate-Na^{+}-rectorite composite microspheres: Preparation, characterization, and dye adsorption. Carbohydr. Polym. 90: 853–858.

Yu, L., J. Gong, C. Zeng, and L. Zhang. 2013a. Preparation of zeolite-A-chitosan hybrid composites and their bioactivities and antimicrobial activities. Mater. Sci. Eng. C 33: 3652–3660.

Yu, X., S. Tong, M. Ge, L. Wu, J. Zuo, C. Cao, and W. Song. 2013b. Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals. J. Environ. Sci. 25: 933–943.

Yuan, W., H. Wu, B. Zheng, X. Zheng, Z. Jiang, X. Hao, and B. Wang, 2007. Sorbitol plasticized chitosan-zeolite hybrid membrane for direct methanol fuel cell. J. Power Sources 172: 604–612.

Zafar, M., M. Ali, S.M. Khan, T. Jamil, and M.T.Z. Butt 2012. Effect of additives on the properties and performance of cellulose acetate derivative membranes in the separation of isopropanol-water mixtures. Desalination 285: 359–365.

Zhan, Y., J. Lin, and J. Li 2013. Preparation and characterization of surfactant-modified hydroxyapatite-zeolite composite and its adsorption behavior toward humic acid and copper(II). Environ. Sci. Pollut. Res. Int. 20: 2512–2526.

Zhou, D., L. Zhang, J. Zhou, and S. Guo. 2004. Cellulose-chitin beads for adsorption of heavy metals in aqueous solution. Water Res. 38: 2643–2650.

Zou, W., H. Bai, L. Zhao, K. Li, and R. Han. 2011. Characterization and properties of zeolite as adsorbent for removal of uranium(VI) from solution in fixed bed column. J. Radioanal. Nucl. Chem. 288: 779–788.

7 Chapter 7: Metal-Impregnated Ion Exchanger for Selective Removal and Recovery of Trace Phosphate

APHA, AWWA, and WEF. 1998. Standard Methods for the Examination of Water and Wastewater (20th edn.). Baltimore, MD: American Public Health Association, American Water Works Association, Water Environment Federation.

Banu, R.J., K.U. Do, and I.T. Yeom. 2008. Phosphorus removal in low alkalinity secondary effluent using alum. Int. J. Environ. Sci. Technol. 5: 93–98.

Blaney, L.M., S. Cinar, and A.K. SenGupta. 2007. Hybrid anion exchanger for trace phosphate removal from water and wastewater. Water Res. 41: 1603–1613.

Chubar, N.I., V.A. Kanibolotskyy, V.V. Strelko, G.G. Gallios, V.F. Samanidou, and T.O. Shaposhnikova. 2005. Adsorption of phosphate ions on novel inorganic ion exchangers. Colloids Surf. A 255: 55–63.

Cooper, P., T. Dee, and G. Yang. 1993. Nutrient removal-methods of meeting the EC urban wastewater directive. In Paper presented at the Fourth Annual Conference on Industrial Wastewater Treatment, Esher, Surrey, March 10, 1993.

Crank, J. 1975. The Mathematics of Diffusion (2nd edn.). Oxford, U.K.: Oxford University Press.

Cumbal, L., J. Greenleaf, D. Leun, and A.K. SenGupta. 2003. Polymer supported inorganic nanoparticles: Characterization and environmental applications. React. Funct. Polym. 54: 167–180.

Cumbal, L. and A.K. SenGupta. 2005. Arsenic removal using polymer-supported hydrated iron(III) oxide nanoparticles: Role of donnan membrane effect. Environ. Sci. Technol. 39: 6508–6515.

Debarbadillo, C., G. Shellswell, W. Cyr, B. Edwards, R. Waite, B. Sabherwal, J. Mullan, and R. Mitchell. 2010. Development of full-scale sizing criteria from tertiary pilot testing results to achieve ultra-low phosphorus limits at Innisfil, Ontario. Proceedings of the 83rd Annual Water Environment Federation Technical Exhibition and Conference, New Orleans, LA, October 2–6, 2010.

DeMarco, M.J., A.K. SenGupta, and J.E. Greenleaf. 2003.

Arsenic removal using a polymeric/ inorganic hybrid sorbent. Water Res. 37: 164-176.

Dzombak, D.A. and F.M. Morel. 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. Hoboken, NJ: John Wiley & Sons, Inc.

Esvelt, L., M. Esvelt, B. Walker, and L. Hendron. 2010. Pilot studies for reducing RPWRF effluent TP for discharge to the Spokane river. Proceedings of the 83rd Annual Water Environment Federation Technical Exhibition and Conference, New Orleans, LA, October 2-6, 2010.

Florida Everglades Forever Act. 1994. Florida Department of Environmental Protection- Office of Ecosystem Projects. Tallahassee, FL.

Galinada, W.A. and H. Yoshida. 2004. Intraparticle diffusion of phosphates in OH-type strongly basic ion exchanger. AIChE J. 50: 2806-2815.

Genz, A., A. Kornmüller, and M. Jekel. 2004. Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide. Water Res. 38: 3523-3530.

Gjerde, D.T. and J.S. Fritz. 1978. Ion Chromatography. New York: A. Hüthig.

Goldman, J.C., K.R. Tenore, and H.I. Stanley. 1973. Inorganic nitrogen removal from wastewater: Effect on phytoplankton growth in coastal marine waters. Science 180: 955-956.

Golterman, H. 1995. Theoretical aspects of the adsorption of ortho-phosphate onto ironhydroxide. Hydrobiologia 315: 59-68.

Hansen, B. 2006. Long-term plan seeks to reduce phosphorus in Spokane river. Civil Eng. 76: 24-25.

Heathwaite, L. and A. Sharpley. 1999. Evaluating measures to control the impact of agricultural phosphorus on water quality. Water Sci. Technol. 39: 149-155.

Helfferich, F.G. 1995. Ion Exchange. Mineola, NY: Dover Publications Inc.

Herring, J.R. and R.J. Fantel. 1993. Phosphate rock demand into the next century: Impact on world food supply. Nat.

Resour. Res. 2: 226-246.

Hiemstra, T. and W. van Riemsdjik. 1999. Surface structural ion adsorption modeling of competitive binding of oxyanions by metal (Hydr)oxides. J. Colloid Interface Sci. 210: 182-193.

Huang, C.P. and L.M. Vane. 1989. Enhancing As 5+ removal by a Fe 2+ -treated activated carbon. Water Pollut. Control Fed. J. 61: 1596-1603.

Jenkins, D. and S.W. Hermanowicz.1991. Principles of chemical phosphorus removal. In: Sedlak, R.I. (ed.), Phosphorus and Nitrogen Removal from Municipal Wastewater: Principles and Practice (2nd edn.). Chelsea, MI: Lewis Publishers.

Jenkins, O., J.F. Fergusson, and A.B. Menar. 1971. Chemical processes for phosphate removal. Water Res. 5: 369-387.

Katsoyiannis, I.A. and A.I. Zouboulis. 2002. Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. Water Res. 36: 5141-5155.

Kuba, T., G.J.F. Smolders, M.C.M. van Loosdrecht, and J.J. Heijnen. 1993. Biological phosphorus removal from wastewater by anaerobic-anoxic sequencing batch reactor. Water Sci. Technol. 27: 241-252.

Liberti, L., G. Boari, D. Petruzzelli, and R. Passino. 1981. Nutrient removal and recovery from wastewater by ion exchange. Water Res. 15: 337-342.

Miltenburg, J. and H. Golterman. 1998. The energy of the adsorption of o-phosphate onto ferric hydroxide. Hydrobiologia 36: 93-97.

Onyango, M.S., H. Matsuda, and T. Ogada. 2003. Sorption kinetics of arsenic onto ironconditioned zeolite. J. Chem. Eng. Jpn. 36: 477-485.

Pandit, A. 2010. Selective removal and recovery of phosphate from wastewater. MS thesis, University of Massachusetts Dartmouth, North Dartmouth, MA.

Rhyther, J.H. and W.M. Dunstan. 1971. Nitrogen, phosphorus, and eutrophication in the coastal marine environment. Science 171: 1008-1013.

Sedlak, R. (ed.). 1991. Phosphorus and Nitrogen Removal from Municipal Wastewater: Principles and Practice. Boca Raton, FL: Lewis Publishers.

Seida, Y. and Y. Nakano. 2002. Removal of phosphate by layered double hydroxides containing iron. Water Res. 36: 1306–1312.

SenGupta, A.K. and D. Zhao. 2000. Selective removal of phosphates and chromates from contaminated water by ion exchange. U.S. Patent 6136199.

Sengupta, S. and A. Pandit. 2011. Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer. Water Res. 45: 3318–3330.

Seviour, R.J., T. Mino, and M. Onuki. 2003. The microbiology of biological phosphorus removal in activated sludge systems. FEMS Microbiol. Rev. 27: 99–127.

Sharpley, A.N., S.C. Chapra, R. Wedepohl, J.T. Sims, T.C. Daniel, and K.R. Reddy. 1994. Managing agricultural phosphorus for protection of surface waters: Issues and options. J. Environ. Qual. 23: 437–451.

Sharpley, A.N., T. Daniel, T. Sims, J. Lemunyon, R. Stevens, and R. Parry. 2003. Agricultural Phosphorus and Eutrophication (2nd edn.). United States Department of Agriculture, Agricultural Research Service.

Stumm, W. and J.J. Morgan. 1995. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters (3rd edn.). New York: John Wiley & Sons.

Szabo, A., I. Takacs, S. Murthy, G.T. Daigger, I. Liksco, and S. Smith. 2008. Significance of design and operational variables in chemical phosphorus removal. Water Environ. Res. 80: 407–416.

Takacs, I., S. Murthy, S. Smith, and M. McGrath. 2006. Chemical phosphorus removal to extremely low levels: Experience of two plants in the Washington, DC area. Water Sci. Technol. 53: 21–28.

Tanada, S., M. Kabayama, N. Kawasaki, T. Sakiyama, T. Nakamura, and M. Araki. 2003. Removal of phosphate by aluminum oxide hydroxide. J. Colloid Interface Sci. 257: 13–140.

USEPA. 1997. Chesapeake Bay Nutrient Reduction Program and

Future Directions. Anapolis, MD: USEPA Chesapeake Bay Program.

USEPA. 2007. Advanced wastewater treatment to achieve low concentration of phosphorus. EPA 910-R-07-002. Seattle, WA.

USGS. 1999. Phosphorus in a Ground-Water Contaminant Plume Discharging to Ashumet Pond, Cape Cod, Massachusetts. Northborough, MA: USGS.

Valiela, I. 1995. Marine Ecological Processes. New York: Springer-Verlag.

Zeng, L., X. Li, and J. Liu. 2004. Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. Water Res. 38: 1318–1326.

Zhao, D. and A.K. SenGupta. 1996. Selective removal and recovery of phosphate in a novel fixed-bed process. Water Sci. Technol. 33: 139–147.

Zhao, D. and A.K. SenGupta. 1998. Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. Water Res. 32: 613–1625.

8 Chapter 8: Molecularly Imprinted Polymers for Water Polishing

Al Abdulgader, H., V. Kochkodan, and N. Hilal. 2013. Hybrid ion exchange—Pressure driven membrane processes in water treatment: A review. Sep. Purif. Technol. 116: 253–264.

Breaken, L. and B. van der Bruggen. 2009. Feasibility of nanofiltration for the removal of endocrine disrupting compounds. Desalination 240: 127–131.

Bryjak, M., J. Wolska, I. Soroko, and N. Kabay. 2009. Adsorption-membrane filtration process in boron removal from first stage seawater RO permeate. Desalination 24: 127–132.

Byun, H.-S., D.-S. Yang, and S.-H. Cho. 2013. Synthesis and characterization of high selective molecularly imprinted polymers for bisphenol A and 2,4-dichlorophenoxyacetic acid by using supercritical fluid technology. Polymer 54: 589–595.

Chahoud, I., A. Gies, M. Paul, G. Schonfelder, and C. Talsness. 2001. Bisphenol A: Low dose effects—High dose effects. Reprod. Toxicol. 15: 587–599.

Chang, L., S. Chen, and X. Li. 2012. Synthesis and properties of core-shell magnetic molecular imprinted polymers. Appl. Surf. Sci. 258: 6660–6664.

Chang, L., Y. Li, J. Chu, J. Qi, and X. Li. 2010. Preparation of core-shell molecularly imprinted polymer via the combination of reversible addition-fragmentation chain transfer polymerization and click reaction. Anal. Chim. Acta 680: 65–71.

Coughlin, J.L., B. Winnik, and B. Buckley. 2011. Measurement of bisphenol A, bisphenol A β-d-glucuronide, genistein, and genistein 4′-β-d-glucuronide via SPE and HPLC-MS/MS. Anal. Bioanal. Chem. 401: 995–1002.

Delgado, L.F., P. Charles, K. Glucina, and C. Morlay. 2012. The removal of endocrine disrupting compounds, pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated carbon—A review. Sci. Total Environ. 435–436: 509–525.

Dudziak, M. and M. Bodzek. 2009. Evaluation of xenoestrogens contents in water by extraction method (in Polish). Ochrona Środowiska 31: 9–14.

Fernandez-Alvarez, P., M. Le Noir, and B. Guieysse. 2009. Removal and destruction of endocrine disrupting contaminants by adsorption with molecularly imprinted polymers followed by simultaneous extraction and phototreatment. J. Hazard. Mater. 163: 1107–1112.

Guler, E., N. Kabay, M. Yuksel, N.O. Yigit, M. Kitis, and M. Bryjak. 2011. Integrated solution for boron removal from seawater using RO process and sorption-membrane filtration hybrid method. J. Membr. Sci. 375: 249–257.

Haginaka, J. and H. Sanbe. 2001. Uniformly sized molecularly imprinted polymer for (S)-naproxen retention and molecular recognition properties in aqueous mobile phase. J. Chromatogr. A 913: 141–146.

Haginaka, J., H. Sanbe, and H. Takehira. 1999b. Uniform-sized molecularly imprinted polymer for (S)-ibuprofen retention properties in aqueous mobile phase. J. Chromatogr. A 857: 117–125.

Haginaka, J., H. Takehira, K. Hosoya, and N. Tanaka. 1999a. Uniform-sized molecularly imprinted polymer for (S)-naproxen selectively modified with hydrophilic external layer. J. Chromatogr. A 849: 331–339.

Higuchi, A., B.-O. Yoon, T. Asano, K. Nakaegawa, S. Miki, M. Hara, Z. He, and I. Pinnau. 2002. Separation of endocrine disruptors from aqueous solutions by pervaporation. J. Membr. Sci. 198: 311–320.

Hosoya, K., K. Yoshizako, Y. Shirasu, K. Kimata, T. Araki, N. Tanaka, and J. Haginaka. 1996. Molecularly imprinted uniform-size polymer-based stationary phase for highperformance liquid chromatography structural contribution of cross-linked polymer network on specific molecular recognition. J. Chromatogr. A 728: 139–147.

Hua, Z., S. Zhou, and M. Zhao. 2009. Fabrication of a surface imprinted hydrogel shell over silica microspheres using bovine serum albumin as a model protein template. Biosens. Bioelectron. 25: 615–622.

Husain, Q. and S. Qayyun. 2013. Biological and enzymatic treatment of bisphenol A and other endocrine disrupting compounds: A review. Crit. Rev. Biotechnol. 33: 260–292.

Ifelebuegu, A.O. 2011. The fate and behavior of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes. Int. J. Environ. Sci. Technol. 8: 245–254.

Joshi, V.P., R.N. Karmalkar, M.G. Kulkarni, and R.A. Mashelkar. 1999. Effect of solvents on selectivity in separation using molecularly imprinted adsorbents: Separation of phenol and bisphenol A. Ind. Eng. Chem. Res. 38: 4417–4423.

Kabay, N. and M. Bryjak. 2013. Hybrid processes combining sorption and membrane filtration. In Encyclopedia of Membrane Science and Technology, E. Hoek and V.V. Tarabara (eds.). New York: John Wiley, pp. 1–21.

Kabay, N., M. Bryjak, S. Schlosser, M. Kitis, S. Avlonitis, Z. Matejka, I. Al-Mutaz, and M. Yuksel. 2008. Adsorption–membrane filtration (AMF) hybrid process for boron removal from seawater: An overview. Desalination 223: 38–48.

Kawaguchi, M., Y. Hayatsu, H. Nakata, Y. Ishii, R. Ito, K. Saito, and H. Nakazawa. 2005. Molecularly imprinted solid phase extraction using stable isotope labeled compounds as template and liquid chromatography–mass spectrometry for trace analysis of bisphenol A in water sample. Anal. Chim. Acta 539: 83–89.

Kempe, H. and M. Kempe. 2004. Novel method for the synthesis of molecularly imprinted polymer bead libraries. Macromol. Rapid Commun. 25: 315–320.

Kempe, H. and M. Kempe. 2006. Development and evaluation of spherical molecularly imprinted polymer beads. Anal. Chem. 78: 3659–3666.

Kitahara, K.-I., I. Yoshihama, T. Hanada, H. Kokuba, and S. Arai. 2010. Synthesis of monodispersed molecularly imprinted polymer particles for high-performance liquid chromatographic separation of cholesterol using templating polymerization in porous silica gel bound with cholesterol molecules on its surface. J. Chromatogr. A 1217: 7249–7254.

Koltuniewicz, A., A. Witek, and K. Bezak. 2004. Efficiency of membrane-sorption integrated processes. J. Membr. Sci. 239: 129–141.

Kruithof, J.C. and B.J. Martijn. 2013. UV/H_2O_2 treatment: An essential process in a multi barrier approach against trace chemical contaminants. Water Sci. Technol. 13: 130–138.

Lee, H.-Y. and B.S. Kim. 2009. Grafting of molecularly imprinted polymers on inifertermodified carbon nanotube. Biosens. Bioelectron. 25: 587–591.

Lee, J., B.C. Lee, J.S. Ra, J. Cho, I.S. Kim, N.I. Chang, H.K. Kim, and S.D. Kim. 2008. Comparison of the removal efficiency of endocrine disrupting compounds in pilot scale sewage treatment processes. Chemosphere 71: 1582–1592.

Margot, J., C. Kienle, A. Magne, M. Weil, L. Rossi, L.F. de Alemcastro, C. Abegglen et al. 2013. Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? Sci. Total Environ. 461–462: 480–498.

Mayes, A.G. and K. Mosbach. 1996. Molecularly imprinted polymer beads: Suspension polymerization using a liquid perfluorocarbon as the dispersing phase. Anal. Chem. 68: 3769–3774.

Omi, S., T. Taguchi, M. Nagai, and G.-H. Ma. 1997. Synthesis of 100 μm uniform porous spheres by SPG emulsification with subsequent swelling of the droplets. J. Appl. Polym. Sci. 63: 931–942.

Prieto, A., A. Vallejo, O. Zuloaga, A. Paschke, B. Sellergen, E. Schillinger, S. Schrader, and M. Möder. 2011. Selective determination of estrogenic compounds in water by microextraction by packed sorbents and a molecularly imprinted polymer coupled with large volume injection-in-port-derivatization gas chromatography–mass spectrometry. Anal. Chim. Acta 703: 41–51.

Sanbe, H. and J. Haginaka. 2002. Uniformly sized molecularly imprinted polymers for bisphenol A and β-estradiol: Retention and molecular recognition properties in hydro-organic mobile phases. J. Pharm. Biomed. 30: 1835–1844.

Sellergren, B. 2001. Molecularly Imprinted Polymers, Vol. 23: Man-Made Mimics of Antibodies and Their Applications in Analytical Chemistry. Amsterdam, the Netherlands: Elsevier.

Shin, H.-S., Ch.-H. Park, S.-J. Park, and H. Pyo. 2001. Sensitive determination of bisphenol A in environmental water by gas chromatography with nitrogen–phosphorus detection after cyanomethylation. J. Chromatogr. A 912: 119–125.

Staples, Ch.A., T.F. Parkerton, and D.R. Peterson. 2000. A risk assessment of selected phthalate esters in North American and Western European surface waters. Chemosphere 40: 885–891.

Sugiura, S., M. Nakajima, and M. Seki. 2002. Preparation of monodispersed polymeric microspheres over 50 μm employing microchannel emulsification. Ind. Eng. Chem. Res. 41: 4043–4047.

Walsh, R., Q. Osmani, H. Hughes, P. Duggan, and P. McLoughlin. 2011. Synthesis of imprinted beads by aqueous suspension polymerization for chiral recognition of antihistamines. J. Chromatogr. B 879: 3523–3530.

Wang, X., L. Chen, X. Xu, and Y. Li. 2011. Synthesis of molecularly imprinted polymers via ring-opening metathesis polymerization for solid-phase extraction of bisphenol A. Anal. Bioanal. Chem. 401: 1423–1432.

Witorsch, R.J. 2002. Endocrine disruptors: Can biological effects and environmental risks be predicted? Reg. Toxicol. Pharmacol. 36: 118–130.

Wolska, J. and M. Bryjak. 2012. Sorption of phthalates on molecularly imprinted polymers. Sep. Sci. Technol. 47: 1316–1321.

Wolska, J. and M. Bryjak. 2014. Removal of bisphenol A by means of hybrid membranesorption process. Sep. Sci. Technol., in press.

Yan, H. and K.H. Row. 2006. Characteristic and synthetic approach of molecularly imprinted polymer. Int. J. Mol. Sci. 7: 155–178.

Yangali-Quitanilla, V., S.K. Maeng, T. Fujioka, M. Kennedy, Z. Li, and G. Amya. 2011. Nanofiltration vs. reverse osmosis for the removal of emerging organic contaminants in water reuse. Des. Water Treat. 34: 50–56.

Ye, L., P.A.G. Cormack, and K. Mosbach. 2001. Molecular imprinting on microgel spheres. Anal. Chim. Acta 435: 187–196.

Yoshimatsu, K., K. Reimhult, A. Krozer, K. Mosbach, K. Sode, and L. Ye. 2007. Uniform molecularly imprinted microspheres and nanoparticles prepared by precipitation polymerization: The control of particle size suitable for different analytical applications. Anal. Chim. Acta 584:

112–121.

Zhang, J.-H., M. Jiang, L. Zou, D. Shi, S.-R. Mei, Y.-X. Zhu, Y. Shi, K. Dai, and B. Lu. 2006. Selective solid-phase extraction of bisphenol A using molecularly imprinted polymers and its application to biological and environmental samples. Anal. Bioanal. Chem. 385: 780–786.

Zhao, Ch., Q. Wei, K. Yang, X. Liu, M. Nomizu, and N. Nishi. 2004. Preparation of porous polysulfone beads for selective removal of endocrine disruptors. Sep. Purif. Technol. 40: 297–302.

Zhu, G., J. Fan, Y. Gao, X. Gao, and J. Wang. 2011. Synthesis of surface molecularly imprinted polymer and the selective solid phase extraction of imidazole from its structural analogues. Talanta 84: 1124–1132.

9 Chapter 9: Biopolymer-Based Sorbents for Metal Sorption

Agulhon, P., V. Markova, M. Robitzer, F. Quignard, and T. Mineva. 2012a. Structure of alginate gels: Interaction of diuronate units with divalent cations from density functional calculations. Biomacromolecules 13: 1899–1907.

Agulhon, P., M. Robitzer, L. David, and F. Quignard. 2012b. Structural regime identification in ionotropic alginate gels: Influence of the cation nature and alginate structure. Biomacromolecules 13: 215–220.

Ahmed, S.R., A.B. Kelly, and T.A. Barbari. 2006. Controlling the orientation of immobilized proteins on an affinity membrane through chelation of a histidine tag to a chitosan-Ni ++ surface. J. Membr. Sci. 280: 553–559.

Ai, L. and J. Jiang. 2013. Catalytic reduction of 4-nitrophenol by silver nanoparticles stabilized on environmentally benign macroscopic biopolymer hydrogel. Bioresour. Technol. 132: 374–377.

Alves, N.M. and J.F. Mano. 2008. Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications. Int. J. Biol. Macromol. 43: 401–414.

Andersen, T., J.E. Melvik, O. Gasered, E. Alsberg, and B.E. Christensen. 2012. Ionically gelled alginate foams: Physical properties controlled by operational and macromolecular parameters. Biomacromolecules 13: 3703–3710.

Arrascue, M.L., H.M. Garcia, O. Horna, and E. Guibal. 2003. Gold sorption on chitosan derivatives. Hydrometallurgy 71: 191–200.

Ayers, P.W., R.G. Parr, and R.G. Pearson. 2006. Elucidating the hard/soft acid/base principle: A perspective based on half-reactions. J. Chem. Phys. 124: 194107.

Ben-Shalom, N. and E. Fallik. 2003. Further suppression of Botrytis cinerea disease in cucumber seedlings by chitosan-copper complex as compared with chitosan alone. Phytoparasitica 31: 99–102.

Boddu, V.M., K. Abburi, J.L. Talbott, E.D. Smith, and R. Haasch. 2008. Removal of arsenic(III) and arsenic(V) from aqueous medium using chitosan-coated biosorbent. Water Res. 42: 633–642.

Campos, K., R. Domingo, T. Vincent, M. Ruiz, A.M. Sastre, and E. Guibal. 2008a. Bismuth recovery from acidic solutions using Cyphos IL-101 immobilized in a composite biopolymer matrix. Water Res. 42: 4019–4031.

Campos, K., T. Vincent, P. Bunio, A. Trochimczuk, and E. Guibal. 2008b. Gold recovery from HCl solutions using Cyphos IL-101 (a quaternary phosphonium ionic liquid) immobilized in biopolymer capsules. Solv. Extr. Ion Exch. 26: 570–601.

Carreon, J., I. Saucedo, R. Navarro, M. Maldonado, R. Guerra, and E. Guibal. 2010. Mercury recovery from aqueous solutions by polymer-enhanced ultrafiltration using a sulfate derivative of chitosan. Membr. Water Treat. 1: 231–251.

Chassary, P., T. Vincent, J.S. Marcano, L.E. Macaskie, and E. Guibal. 2005. Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives. Hydrometallurgy 76: 131–147.

Chen, J.P., L.A. Hong, S.N. Wu, and L. Wang. 2002. Elucidation of interactions between metal ions and Ca alginate-based ion-exchange resin by spectroscopic analysis and modeling simulation. Langmuir 18: 9413–9421.

Chen, Y., J. Hu, and J. Wang. 2012. Kinetics and thermodynamics of Cu(II) biosorption on to a novel magnetic chitosan composite bead. Environ. Technol. 33: 2345–2351.

Cheng, Y., X. Luo, J. Betz, G.F. Payne, W.E. Bentley, and G.W. Rubloff. 2011. Mechanism of anodic electrodeposition of calcium alginate. Soft Matter 7: 5677–5684.

Christensen, B.E., M. Indergaard, and O. Smidsrod. 1990. Polysaccharide research in Trondheim. Carbohydr. Polym. 13: 239–255.

Chtchigrovsky, M., Y. Lin, K. Ouchaou, M. Chaumontet, M. Robitzer, F. Quignard, and F. Taran. 2012. Dramatic effect of the gelling cation on the catalytic performances of alginate-supported palladium nanoparticles for the Suzuki-Miyaura reaction. Chem. Mater. 24: 1505–1510.

Chtchigrovsky, M., A. Primo, P. Gonzalez, K. Molvinger, M. Robitzer, F. Quignard, and F. Taran. 2009. Functionalized chitosan as a green, recyclable, biopolymer-supported catalyst for the 3+2 Huisgen cycloaddition. Angew. Chem. Int. Ed. 48: 5916–5920.

Condi de Godoi, F., R.B. Rabelo, F.d.C. Vasconcellos, and M.M. Beppu. 2011. Preparation of copper nanoparticles in chitosan membranes and their application as irreversible humidity indicators, in Pierucci, S. (ed.), Icheap-10: 10th International Conference on Chemical and Process Engineering. Italian Association of Chemical Engineering, Milano, Italy. Pts 1–3, pp. 217–222.

Condi de Godoi, F., E. Rodriguez-Castellon, E. Guibal, and M.M. Beppu. 2013. An XPS study of chromate and vanadate sorption mechanism by chitosan membrane containing copper nanoparticles. Chem. Eng. J. 234: 423–429.

Corma, A., P. Concepcion, I. Dominguez, V. Fornes, and M.J. Sabater. 2007. Gold supported on a biopolymer (chitosan) catalyzes the regioselective hydroamination of alkynes. J. Catal. 251: 39–47.

Cuadros, T.R., O. Skurtys, and J.M. Aguilera. 2012. Mechanical properties of calcium alginate fibers produced with a microfluidic device. Carbohydr. Polym. 89: 1198–1206.

Czulak, J., C. Jouannin, T. Vincent, I. Dez, A.C. Gaumont, and E. Guibal. 2012. Nitrophenol hydrogenation using Pd immobilized on ionic liquid alginate spherical resins. Sep. Sci. Technol. 47: 2166–2176.

Dambies, L., E. Guibal, and A. Roze. 2000. Arsenic(V) sorption on molybdate-impregnated chitosan beads. Colloids Surf. A 170: 19–31.

Dambies, L., T. Vincent, A. Domard, and E. Guibal. 2001. Preparation of chitosan gel beads by ionotropic molybdate gelation. Biomacromolecules 2: 1198–1205.

Dambies, L., T. Vincent, and E. Guibal. 2002. Treatment of arsenic-containing solutions using chitosan derivatives: Uptake mechanism and sorption performances. Water Res. 36: 3699–3710.

Davis, T.A., B. Volesky, and A. Mucci. 2003. A review of the biochemistry of heavy metal biosorption by brown algae. Water Res. 37: 4311–4330.

Desorme, M., A. Montembault, J.-M. Lucas, C. Rochas, T. Bouet, and L. David. 2013. Spinning of hydroalcoholic chitosan solutions. Carbohydr. Polym. 98: 50–63.

Deze, E.G., S.K. Papageorgiou, E.P. Favvas, and F.K. Katsaros. 2012. Porous alginate aerogel beads for effective and rapid heavy metal sorption from aqueous solutions: Effect of porosity in Cu 2+ and Cd 2+ ion sorption. Chem. Eng. J. 209: 537–546.

Dresvyanina, E.N., I.P. Dobrovol'skaya, P.V. Popryadukhin, V.E. Yudin, E.M. Ivan'kova, V.Y. Elokhovskii, and A.Y. Khomenko. 2013. Influence of spinning conditions on properties of chitosan fibers. Fibre Chem. 44: 280–283.

Dzul Erosa, M.S., T.I. Saucedo Medina, R. Navarro Mendoza, M. Avila Rodriguez, and E. Guibal. 2001. Cadmium sorption on chitosan sorbents: Kinetic and equilibrium studies. Hydrometallurgy 61: 157–167.

Escudero, C., N. Fiol, I. Villaescusa, and J.-C. Bollinger. 2009. Arsenic removal by a waste metal (hydr)oxide entrapped into calcium alginate beads. J. Hazard. Mater. 164: 533–541.

Fatin-Rouge, N., A. Dupont, A. Vidonne, J. Dejeu, P. Fievet, and A. Foissy. 2006. Removal of some divalent cations from water by membrane-filtration assisted with alginate. Water Res. 40: 1303–1309.

Gonzalez Bermudez, Y., I.L. Rodriguez Rico, E. Guibal, M. Calero de Hoces, and M. Angeles Martin-Lara. 2012. Biosorption of hexavalent chromium from aqueous solution by Sargassum muticum brown alga. Application of statistical design for process optimization. Chem. Eng. J. 183: 68–76.

Guibal, E. 2004. Interactions of metal ions with chitosan-based sorbents: A review. Sep. Purif. Technol. 38: 43–74.

Guibal, E. 2005. Heterogeneous catalysis on chitosan-based materials: A review. Prog. Polym. Sci. 30: 71–109.

Guibal, E., S. Cambe, S. Bayle, J.-M. Taulemesse, and T. Vincent. 2013. Silver/chitosan/ cellulose fibers foam composites: From synthesis to antibacterial properties. J. Colloid Interface Sci. 393: 411–420.

Guibal, E., L. Dambies, C. Milot, and J. Roussy. 1999a. Influence of polymer structural parameters and experimental conditions on metal anion sorption by chitosan. Polym. Int. 48: 671–680.

Guibal, E., A. Figuerola Pinol, M. Ruiz, T. Vincent, C. Jouannin, and A.M. Sastre. 2010. Immobilization of Cyphos ionic liquids in alginate capsules for Cd(II) sorption. Sep. Sci. Technol. 45: 1935–1949.

Guibal, E., K.C. Gavilan, P. Bunio, T. Vincent, and A. Trochimczuk. 2008. Cyphos IL 101 (tetradecyl(trihexyl)phosphonium chloride) immobilized in biopolymer capsules for Hg(II) recovery from HCl solutions. Sep. Sci. Technol. 43: 2406–2433.

Guibal, E., A. Larkin, T. Vincent, and J.M. Tobin. 1999b. Chitosan sorbents for platinum sorption from dilute solutions. Ind. Eng. Chem. Res. 38: 4011–4022.

Guibal, E., C. Milot, O. Eterradossi, C. Gauf�er, and A. Domard. 1999c. Study of molybdate ion sorption on chitosan gel beads by different spectrometric analyses. Int. J. Biol. Macromol. 24: 49–59.

Guibal, E., C. Milot, and J. Roussy. 1999d. Molybdate sorption by cross-linked chitosan beads: Dynamic studies. Water Environ. Res. 71: 10–17.

Guibal, E., C. Milot, and J. Roussy. 2000a. In�uence of hydrolysis mechanisms on molybdate sorption isotherms using chitosan. Sep. Sci. Technol. 35: 1021–1038.

Guibal, E., C. Milot, and J.M. Tobin. 1998. Metal-anion sorption by chitosan beads: Equilibrium and kinetic studies. Ind. Eng. Chem. Res. 37: 1454–1463.

Guibal, E., C. Roulph, and P. Lecloirec. 1992. Uranium biosorption by a �lamentous fungus Mucor miehei—pH effect on mechanisms and performances of uptake. Water Res. 26: 1139–1145.

Guibal, E., C. Roulph, and P. Lecloirec. 1995. Infrared spectroscopic study of uranyl biosorption by fungal biomass and materials of biological origin. Environ. Sci. Technol. 29: 2496–2503.

Guibal, E., M. Ruiz, T. Vincent, A. Sastre, and R. Navarro-Mendoza. 2001. Platinum and palladium sorption on chitosan derivatives. Sep. Sci. Technol. 36: 1017–1040.

Guibal, E., I. Saucedo, J. Roussy and P. Lecloirec. 1994. Uptake of uranyl ions by new sorbing polymers—Discussion of adsorption isotherms and pH effect. React. Polym. 23: 147–156.

Guibal, E., N.V. Sweeney, T. Vincent, and J.M. Tobin. 2002. Sulfur derivatives of chitosan for palladium sorption. React. Funct. Polym. 50: 149–163.

Guibal, E. and T. Vincent. 2004. Chitosan-supported palladium catalyst. IV. Influence of temperature on nitrophenol degradation and thermodynamic parameters. J. Environ. Manage. 71: 15–23.

Guibal, E. and T. Vincent. 2006. Palladium recovery from dilute effluents using biopolymerimmobilized extractant. Sep. Sci. Technol. 41: 2533–2553.

Guibal, E., T. Vincent, and F. Peirano Blondet. 2007. Biopolymers as supports for heterogeneous catalysis: Focus on chitosan, a promising aminopolysaccharide, in Sengupta, A.K. (ed.), Ion Exchange and Solvent Extraction. CRC Press, Boca Raton, FL. Vol. 18, pp. 151–292.

Guibal, E., T. Vincent, and C. Jouannin. 2009. Immobilization of extractants in biopolymer capsules for the synthesis of new resins: A focus on the encapsulation of tetraalkyl phosphonium ionic liquids. J. Mater. Chem. 19: 8515–8527.

Guibal, E., T. Vincent, and R.N. Mendoza. 2000b. Synthesis and characterization of a thiourea derivative of chitosan for platinum recovery. J. Appl. Polym. Sci. 75: 119–134.

Guibal, E., T. Vincent, and S. Spinelli. 2005. Environmental application of chitosan-supported catalysts: Catalytic hollow fibers for the degradation of phenolic derivatives. Sep. Sci. Technol. 40: 633–657.

Guibal, E., T. Vincent, E. Touraud, S. Colombo, and A. Ferguson. 2006. Oxidation of hydroquinone to p-benzoquinone catalyzed by Cu(II) supported on chitosan flakes. J. Appl. Polym. Sci. 100: 3034–3043.

Gupta, A., V.S. Chauhan, and N. Sankararamakrishnan. 2009. Preparation and evaluation of iron-chitosan composites for removal of As(III) and As(V) from arsenic contaminated real life groundwater. Water Res. 43: 3862–3870.

Guzman, J., I. Saucedo, R. Navarro, J. Revilla, and E. Guibal. 2002. Vanadium interactions with chitosan: Influence of polymer protonation and metal speciation. Langmuir 18: 1567–1573.

Guzman, J., I. Saucedo, J. Revilla, R. Navarro, and E. Guibal. 2003. Copper sorption by chitosan in the presence of citrate ions: Influence of metal speciation on sorption mechanism and uptake capacities. Int. J. Biol. Macromol. 33: 57–65.

Hernandez-Carmona, G., D.J. McHugh, D.L. Arvizu-Higuera, and Y.E. RodriguezMontesinos. 1998. Pilot plant scale extraction of alginate from Macrocystis pyrifera. 1. Effect of pre-extraction treatments on yield and quality of alginate. J. Appl. Phycol. 10: 507–513.

Hernandez-Carmona, G., D.J. McHugh, and F. Lopez-Gutierrez. 1999. Pilot plant scale extraction of alginates from Macrocystis pyrifera. 2. Studies on extraction conditions and methods of separating the alkaline-insoluble residue. J. Appl. Phycol. 11: 493–502.

Hernandez, R.B., O.R. Yola, and A.L.R. Merce. 2007. Chemical equilibrium in the complexation of first transition series divalent cations Cu 2+ , Mn 2+ and Zn 2+ with chitosan. J. Braz. Chem. Soc. 18: 1388–1396.

Hoang Vinh, T., T. Lam Dai, B. Cham Thi, V. Hoang Dinh, N. Thinh Ngoc, P. Dien Gia, and N. Phuc Xuan. 2010. Synthesis, characterization, antibacterial and antiproliferative activities of monodisperse chitosan-based silver nanoparticles. Colloids Surf. A 360: 32–40.

Hortigueela, M.J., I. Aranaz, M.C. Gutierrez, M. Luisa Ferrer, and F. del Monte. 2011. Chitosan gelation induced by the in situ formation of gold nanoparticles and its processing into macroporous scaffolds. Biomacromolecules 12: 179–186.

Horzum, N., M.M. Demir, M. Nairat, and T. Shahwan. 2013. Chitosan fiber-supported zerovalent iron nanoparticles as a novel sorbent for sequestration of inorganic arsenic. RSC Adv. 3: 7828–7837.

Jansson-Charrier, M., E. Guibal, J. Roussy, B. Delanghe, and P. LeCloirec. 1996a. Vanadium (IV) sorption by chitosan: Kinetics and equilibrium. Water Res. 30: 465–475.

Jansson-Charrier, M., E. Guibal, J. Roussy, R. Surjous, and P. LeCloirec. 1996b. Dynamic removal of uranium by chitosan: Influence of operating parameters. Water Sci. Technol. 34: 169–177.

Jaworska, M., K. Kula, P. Chassary, and E. Guibal. 2003a.

Influence of chitosan characteristics on polymer properties: II. Platinum sorption properties. Polym. Int. 52: 206–212.

Jaworska, M., K. Sakurai, P. Gaudon, and E. Guibal. 2003b. Influence of chitosan characteristics on polymer properties. I: Crystallographic properties. Polym. Int. 52: 198–205.

Jena, P., S. Mohanty, R. Mallick, B. Jacob, and A. Sonawane. 2012. Toxicity and antibacterial assessment of chitosan-coated silver nanoparticles on human pathogens and macrophage cells. Int. J. Nanomed. 7: 1805–1818.

Jeon, C. and W.H. Holl. 2004. Application of the surface complexation model to heavy metal sorption equilibria onto aminated chitosan. Hydrometallurgy 71: 421–428.

Jodra, Y. and F. Mijangos. 2001. Ion exchange selectivities of calcium alginate gels for heavy metals. Water Sci. Technol. 43: 237–244.

Jouannin, C., I. Dez, A.C. Gaumont, J.M. Taulemesse, T. Vincent, and E. Guibal. 2011. Palladium supported on alginate/ionic liquid highly porous monoliths: Application to 4-nitroaniline hydrogenation. Appl. Catal. B 103: 444–452.

Jouannin, C., C. Vincent, I. Dez, A.-C. Gaumont, T. Vincent, and E. Guibal. 2013. Highly porous catalytic materials with Pd and ionic liquid supported on chitosan. J. Appl. Polym. Sci. 128: 3122–3130.

Juang, R.S. and C.Y. Ju. 1997. Equilibrium sorption of copper(II)-ethylenediaminetetraacetic acid chelates onto cross-linked, polyaminated chitosan beads. Ind. Eng. Chem. Res. 36: 5403–5409.

Juang, R.S., F.C. Wu, and R.L. Tseng. 1999. Adsorption removal of copper(II) using chitosan from simulated rinse solutions containing chelating agents. Water Res. 33: 2403–2409.

Kamari, A. and W.S.W. Ngah. 2009. Isotherm, kinetic and thermodynamic studies of lead and copper uptake by H_2SO_4 modified chitosan. Colloids Surf. B 73: 257–266.

Kannamba, B., K.L. Reddy, and B.V. AppaRao. 2010. Removal of Cu(II) from aqueous solutions using chemically modified chitosan. J. Hazard. Mater. 175: 939–948.

Karagunduz, A. and D. Unal. 2006. New method for evaluation of heavy metal binding to alginate beads using pH and conductivity data. Adsorption 12: 175–184.

Khotimchenko, M., V. Kovalev, and Y. Khotimchenko. 2008. Comparative equilibrium studies of sorption of Pb(II) ions by sodium and calcium alginate. J. Environ. Sci. 20: 827–831.

Khun, K., Z.H. Ibupoto, J. Lu, M.S. AlSalhi, M. Atif, A.A. Ansari, and M. Willander. 2012. Potentiometric glucose sensor based on the glucose oxidase immobilized iron ferrite magnetic particle/chitosan composite modi�ed gold coated glass electrode. Sens. Actuators B 173: 698–703.

Kica, M., T. Vincent, A. Trochimczuk, R. Navarro, and E. Guibal. 2014. Tetraalkylphosphonium ionic liquid encapsulation in alginate beads for Cd(II) sorption from HCl solutions. Solv. Extr. Ion Exch., in press.

Kleinuebing, S.J., E.A. da Silva, M.G.C. da Silva, and E. Guibal. 2011. Equilibrium of Cu(II) and Ni(II) biosorption by marine alga Sargassum filipendula in a dynamic system: Competitiveness and selectivity. Bioresour. Technol. 102: 4610–4617.

Kleinuebing, S.J., R.S. Vieira, M.M. Beppu, E. Guibal, and M.G. Carlos da Silva. 2010. Characterization and evaluation of copper and nickel biosorption on acidic algae Sargassum filipendula. Mater. Res. 13: 541–550.

Kolodynska, D. 2012. Adsorption characteristics of chitosan modi�ed by chelating agents of a new generation. Chem. Eng. J. 179: 33–43.

Kramareva, N.V., E.D. Finashina, A.V. Kucherov, and L.M. Kustov. 2003. Copper complexes stabilized by chitosans: Peculiarities of the structure, redox, and catalytic properties. Kinet. Catal. 44: 793–800.

Kramareva, N.V., A.Y. Stakheev, O.P. Tkachenko, K.V. Klementiev, W. Grunert, E.D. Finashina, and L.M. Kustov. 2004. Heterogenized palladium chitosan complexes as potential catalysts in oxidation reactions: Study of the structure. J. Mol. Catal. A 209: 97–106.

Krys, P., F. Testa, A. Trochimczuk, C. Pin, J.M. Taulemesse, T. Vincent, and E. Guibal. 2013. Encapsulation of ammonium molybdophosphate and zirconium phosphate in alginate matrix for the sorption of rubidium(I). J.

Colloid Interface Sci. 409: 141–150.

Kucherov, A., E. Finashina, N. Kramareva, V. Rogacheva, A. Zezin, E. Said-Galiyev, and L. Kustov. 2003. Comparative study of Cu(II) catalytic sites immobilized onto different polymeric supports. Macromol. Symp. 204: 175–189.

Kuncoro, E.P., J. Roussy, and E. Guibal. 2005. Mercury recovery by polymer-enhanced ultrafiltration: Comparison of chitosan and poly(ethylenimine) used as macroligand. Sep. Sci. Technol. 40: 659–684.

Lavertu, M., V. Darras, and M.D. Buschmann. 2012. Kinetics and efficiency of chitosan reacetylation. Carbohydr. Polym. 87: 1192–1198.

Leonhardt, S.E.S., A. Stolle, B. Ondruschka, G. Cravotto, C. De Leo, K.D. Jandt, and T.F. Keller. 2010. Chitosan as a support for heterogeneous Pd catalysts in liquid phase catalysis. Appl. Catal. A 379: 30–37.

Lezehari, M., J.-P. Basly, M. Baudu, and O. Bouras. 2010. Alginate encapsulated pillared clays: Removal of a neutral/anionic biocide (pentachlorophenol) and a cationic dye (safranine) from aqueous solutions. Colloids Surf. A 366: 88–94.

Li, C., W. Li, and L. Wei. 2012a. Removal of ammonia from aqueous solution using copperincorporated chitosan. Energy Educ. Sci. Technol. A 30: 223–230.

Li, D., J. Diao, J. Zhang, and J. Liu. 2011. Fabrication of new chitosan-based composite sponge containing silver nanoparticles and its antibacterial properties for wound dressing. J. Nanosci. Nanotechnol. 11: 4733–4738.

Li, L., Y. Fang, R. Vreeker, and I. Appelqvist. 2007. Reexamining the egg-box model in calcium-alginate gels with X-ray diffraction. Biomacromolecules 8: 464–468.

Li, Y., F. Wang, F. Huang, Y. Li, and S. Feng. 2012b. Direct electrochemistry of glucose oxidase and its biosensing to glucose based on the Chit-MWCNTs-AuNRs modified gold electrode. J. Electroanal. Chem. 685: 86–90.

Lian, W., S. Liu, J. Yu, X. Xing, J. Li, M. Cui, and J. Huang. 2012. Electrochemical sensor based on gold nanoparticles fabricated molecularly imprinted polymer film at chitosanplatinum nanoparticles/graphene-gold nanoparticles double nanocomposites modified electrode for detection of erythromycin. Biosens. Bioelectron. 38: 163–169.

Lim, J.-W. and I.-J. Kang. 2013. Chitosan-gold nano composite for dopamine analysis using Raman scattering. Bull. Korean Chem. Soc. 34: 237–242.

Liu, B., Y. Deng, X. Hu, Z. Gao, and C. Sun. 2012. Electrochemical sensing of trichloroacetic acid based on silver nanoparticles doped chitosan hydrogel film prepared with controllable electrodeposition. Electrochim. Acta 76: 410–415.

Macquarrie, D.J. and J.J.E. Hardy. 2005. Applications of functionalized chitosan in catalysis. Ind. Eng. Chem. Res. 44: 8499–8520.

Madihally, S.V. and H.W.T. Matthew. 1999. Porous chitosan scaffolds for tissue engineering. Biomaterials 20: 1133–1142.

Martina, K., S.E.S. Leonhardt, B. Ondruschka, M. Curini, A. Binello, and G. Cravotto. 2011. In situ cross-linked chitosan Cu(I) or Pd(II) complexes as a versatile, eco-friendly recyclable solid catalyst. J. Mol. Catal. A 334: 60–64.

Mathew, M., S. Sureshkumar, and N. Sandhyarani. 2012. Synthesis and characterization of gold-chitosan nanocomposite and application of resultant nanocomposite in sensors. Colloids Surf. B 93: 143–147.

McHugh, D.J., G. Hernandez-Carmona, D. Luz Arvizu-Higuera, and Y.E. RodriguezMontesinos. 2001. Pilot plant scale extraction of alginates from Macrocystis pyrifera—3. Precipitation, bleaching and conversion of calcium alginate to alginic acid. J. Appl. Phycol. 13: 471–479.

Milot, C., J. McBrien, S. Allen, and E. Guibal. 1998. Influence of physicochemical and structural characteristics of chitosan flakes on molybdate sorption. J. Appl. Polym. Sci. 68: 571–580.

Mimura, H., M. Saito, K. Akiba, and Y. Onodera. 2001. Selective uptake of cesium by ammonium molybdophosphate (AMP)-calcium alginate composites. J. Nucl. Sci. Technol. 38: 872–878.

Mimura, H., W. Yan, Y. Wang, Y. Niibori, I. Yamagishi, M. Ozawa, T. Ohnishi, and S. Koyama. 2011. Selective separation and recovery of cesium by ammonium tungstophosphatealginate microcapsules. Nucl. Eng. Des. 241: 4750–4757.

Mirmohseni, A., M.S.S. Dorraji, A. Figoli, and F. Tasselli. 2012. Chitosan hollow fibers as effective biosorbent toward dye: Preparation and modeling. Bioresour. Technol. 121: 212–220.

Modrzejewska, Z. and W. Eckstein. 2004. Chitosan hollow fiber membranes. Biopolymers 73: 61–68.

Modrzejewska, Z. and W. Kaminski. 1999. Separation of Cr(VI) on chitosan membranes. Ind. Eng. Chem. Res. 38: 4946–4950.

Mori, Y., T. Ono, Y. Miyahira, N. Vinh Quang, T. Matsui, and M. Ishihara. 2013. Antiviral activity of silver nanoparticle/chitosan composites against H1N1 influenza A virus. Nanoscale Res. Lett. 8: 93.

Moucel, R., K. Perrigaud, J.-M. Goupil, P.-J. Madec, S. Marinel, E. Guibal, A.-C. Gaumont, and I. Dez. 2010. Importance of the conditioning of the chitosan support in a catalystcontaining ionic liquid phase immobilised on chitosan: The palladium-catalysed allylation reaction case. Adv. Synth. Catal. 352: 433–439.

Ngomsik, A.-F., A. Bee, J.-M. Siaugue, D. Talbot, V. Cabuil, and G. Cote. 2009. Co(II) removal by magnetic alginate beads containing Cyanex 272. J. Hazard. Mater. 166: 1043–1049.

Nishad, P.A., A. Bhaskarapillai, S. Velmurugan, and S.V. Narasimhan 2012. Cobalt (II) imprinted chitosan for selective removal of cobalt during nuclear reactor decontamination. Carbohydr. Polym. 87: 2690–2696.

Notin, L., C. Viton, L. David, P. Alcouffe, C. Rochas, and A. Domard. 2006a. Morphology and mechanical properties of chitosan fibers obtained by gel-spinning: Influence of the dryjet-stretching step and ageing. Acta Biomater. 2: 387–402.

Notin, L., C. Viton, J.-M. Lucas, and A. Domard. 2006b. Pseudo-dry-spinning of chitosan. Acta Biomater. 2: 297–311.

Osifo, P.O., H.W.J.P. Neomagus, R.C. Everson, A. Webster, and M.A.v. Gun. 2009. The adsorption of copper in a packed-bed of chitosan beads: Modeling, multiple adsorption and regeneration. J. Hazard. Mater. 167: 1242–1245.

Padala, A.N., A. Bhaskarapillai, S. Velmurugan, and S.V. Narasimhan. 2011. Sorption behaviour of Co(II) and Cu(II) on chitosan in presence of nitrilotriacetic acid. J. Hazard. Mater. 191: 110–117.

Papageorgiou, S.K., F.K. Katsaros, E.P. Kouvelos, J.W. Nolan, H. Le Deit, and N.K. Kanellopoulos. 2006. Heavy metal sorption by calcium alginate beads from Laminaria digitata. J. Hazard. Mater. 137: 1765–1772.

Park, S.-I., I.S. Kwak, S.W. Won, and Y.-S. Yun. 2013. Glutaraldehyde-crosslinked chitosan beads for sorptive separation of Au(III) and Pd(II): Opening a way to design reductioncoupled selectivity-tunable sorbents for separation of precious metals. J. Hazard. Mater. 248: 211–218.

Patale, R.L. and V.B. Patravale. 2011. O,N-carboxymethyl chitosan-zinc complex: A novel chitosan complex with enhanced antimicrobial activity. Carbohydr. Polym. 85: 105–110.

Payne, G.F. 2007. Biopolymer-based materials: The nanoscale components and their hierarchical assembly. Curr. Opin. Chem. Biol. 11: 214–219.

Pearson, R.G. 1966. Acids and bases. Science (New York, N.Y.) 151(3707): 172–177.

Peirano Blondet, F., T. Vincent, and E. Guibal. 2008. Hydrogenation of toluene using palladium supported on chitosan hollow fiber: Catalyst characterization and influence of operative parameters studied by experimental design methodology. Int. J. Biol. Macromol. 43: 69–78.

Pielesz, A. and M.K.K. Bak. 2008. Raman spectroscopy and WAXS method as a tool for analysing ion-exchange properties of alginate hydrogels. Int. J. Biol. Macromol. 43: 438–443.

Pillai, C.K.S., W. Paul, and C.P. Sharma. 2009. Chitin and chitosan polymers: Chemistry, solubility and fiber formation. Prog. Polym. Sci. 34: 641–678.

Piron, E., M. Accominotti, and A. Domard. 1997. Interaction between chitosan and uranyl ions. Role of physical and physicochemical parameters on the kinetics of sorption.

Langmuir 13: 1653–1658.

Piron, E. and A. Domard. 1997. Interaction between chitosan and uranyl ions—Part 1. Role of physicochemical parameters. Int. J. Biol. Macromol. 21: 327–335.

Piron, E. and A. Domard. 1998a. Formation of a ternary complex between chitosan and ion pairs of strontium carbonate. Int. J. Biol. Macromol. 23: 113–120.

Piron, E. and A. Domard. 1998b. Interaction between chitosan and uranyl ions. Part 2. Mechanism of interaction. Int. J. Biol. Macromol. 22: 33–40.

Plazinski, W. 2012. Sorption of lead, copper, and cadmium by calcium alginate. Metal binding stoichiometry and the pH effect. Environ. Sci. Pollut. Res. 19: 3516–3524.

Plazinski, W. 2013. Binding of heavy metals by algal biosorbents. Theoretical models of kinetics, equilibria and thermodynamics. Adv. Colloid Interface Sci. 197–198: 58–67.

Portero, A., C. Remunan-Lopez, M.T. Criado, and M.J. Alonso. 2002. Reacetylated chitosan microspheres for controlled delivery of anti-microbial agents to the gastric mucosa. J. Microencapsul. 19: 797–809.

Qin, Y., C. Zhu, J. Chen, D. Liang, and G. Wo. 2007. Absorption and release of zinc and copper ions by chitosan fibers. J. Appl. Polym. Sci. 105: 527–532.

Quignard, F., F. Di Renzo, and E. Guibal. 2010. From natural polysaccharides to materials for catalysis, adsorption, and remediation, in Rauter, A.P., Vogel, P., and Queneau, Y. (eds.), Carbohydrates in Sustainable Development I: Renewable Resources for Chemistry and Biotechnology. Springer, pp. 165–197.

Rabelo, R.B., R.S. Vieira, F.M.T. Luna, E. Guibal, and M.M. Beppu. 2012. Adsorption of copper(II) and mercury(II) ions onto chemically-modified chitosan membranes: Equilibrium and kinetic properties. Adsorpt. Sci. Technol. 30: 1–21.

Rhazi, M., J. Desbrieres, A. Tolaimate, M. Rinaudo, P. Vottero, A. Alagui, and M. El Meray. 2002. Influence of the nature of the metal ions on the complexation with chitosan. Application to the treatment of liquid waste. Eur. Polym. J. 38: 1523–1530.

Rivas, B.L., E. Pereira, R. Cid, and K.E. Geckeler. 2005. Polyelectrolyte-assisted removal of metal ions with ultrafiltration. J. Appl. Polym. Sci. 95: 1091–1099.

Roberts, G.A.F. 1992. Chitin Chemistry. The Macmillan Press Limited, London, U.K.

Rodrigues, J.R. and R. Lagoa. 2006. Copper ions binding in Cu-alginate gelation. J. Carbohydr. Chem. 25: 219–232.

Ruiz, M., A.M. Sastre, and E. Guibal. 2000. Palladium sorption on glutaraldehyde-crosslinked chitosan. React. Funct. Polym. 45: 155–173.

Ruiz, M., A.M. Sastre, and E. Guibal. 2002. Pd and Pt recovery using chitosan gel beads. I. Influence of the drying process on diffusion properties. Sep. Sci. Technol. 37: 2143–2166.

Ruiz, M., A.M. Sastre, M.C. Zikan, and E. Guibal. 2001. Palladium sorption on glutaraldehydecrosslinked chitosan in fixed-bed systems. J. Appl. Polym. Sci. 81: 153–165.

Santos Sopena, L.A., M. Ruiz, A.V. Pestov, A.M. Sastre, Y. Yatluk, and E. Guibal. 2011. N-(2-(2-Pyridyl)ethyl)chitosan (PEC) for Pd(II) and Pt(IV) sorption from HCl solutions. Cellulose 18: 309–325.

Saravanan, S., S. Nethala, S. Pattnaik, A. Tripathi, A. Moorthi, and N. Selvamurugan. 2011. Preparation, characterization and antimicrobial activity of a bio-composite scaffold containing chitosan/nano-hydroxyapatite/nano-silver for bone tissue engineering. Int. J. Biol. Macromol. 49: 188–193.

Sarkar, S., E. Guibal, F. Quignard, and A.K. SenGupta. 2012. Polymer-supported metals and metal oxide nanoparticles: Synthesis, characterization, and applications. J. Nanopart. Res. 14: 715.

Schuessler, S., N. Blaubach, A. Stolle, G. Cravotto, and B. Ondruschka. 2012. Application of a cross-linked Pd-chitosan catalyst in liquid-phase-hydrogenation using molecular hydrogen. Appl. Catal. A 445: 231–238.

Shinde, R.N., A.K. Pandey, R. Acharya, R. Guin, S.K. Das, N.S. Rajurkar, and P.K. Pujari. 2013. Chitosan-transition metal ions complexes for selective arsenic(V) preconcentration. Water Res. 47: 3497–3506.

Sicupira, D., K. Campos, T. Vincent, V. Leao, and E. Guibal. 2010. Palladium and platinum sorption using chitosan-based hydrogels. Adsorption 16: 127–139.

Sikorski, P., F. Mo, G. Skjak-Braek, and B.T. Stokke. 2007. Evidence for egg-box-compatible interactions in calcium-alginate gels from fiber X-ray diffraction. Biomacromolecules 8: 2098–2103.

Singh, P., J. Bajpai, A.K. Bajpai, and R.B. Shrivastava. 2011. Fixed-bed studies on removal of arsenic from simulated aqueous solutions using chitosan nanoparticles. Bioremed. J. 15: 148–156.

Sorlier, P., A. Denuziere, C. Viton, and A. Domard. 2001. Relation between the degree of acetylation and the electrostatic properties of chitin and chitosan. Biomacromolecules 2: 765–772.

Sugunan, A., C. Thanachayanont, J. Dutta, and J.G. Hilborn. 2005. Heavy-metal ion sensors using chitosan-capped gold nanoparticles. Sci. Technol. Adv. Mater. 6: 335–340.

Svecova, L., M. Spanelova, M. Kubal, and E. Guibal. 2006. Cadmium, lead and mercury biosorption on waste fungal biomass issued from fermentation industry. 1. Equilibrium studies. Sep. Purif. Technol. 52: 142–153.

Tasselli, F., A. Mirmohseni, M.S. Seyed Dorraji, and A. Figoli. 2013. Mechanical, swelling and adsorptive properties of dry-wet spun chitosan hollow fibers crosslinked with glutaraldehyde. React. Funct. Polym. 73: 218–223.

Thomas, V., M.M. Yallapu, B. Sreedhar, and S.K. Bajpai. 2009. Fabrication, characterization of chitosan/nanosilver lm and its potential antibacterial application. J. Biomater. Sci. Polym. Ed. 20: 2129–2144.

Tian, L., Y. Feng, Y. Qi, B. Wang, Y. Chen, and X. Fu. 2012. Non-enzymatic amperometric sensor for hydrogen peroxide based on a biocomposite made from chitosan, hemoglobin, and silver nanoparticles. Microchim. Acta 177: 39–45.

Tseng, R.L., F.C. Wu, and R.S. Juang. 1999. Effect of complexing agents on liquid-phase adsorption and desorption of copper(II) using chitosan. J. Chem. Technol. Biotechnol. 74: 533–538.

Varma, A.J., S.V. Deshpande, and J.F. Kennedy. 2004 Metal complexation by chitosan and its derivatives: A review. Carbohydr. Polym. 55: 77–93.

Vieira, R.S. and M.M. Beppu. 2006. Interaction of natural and crosslinked chitosan membranes with Hg(II) ions. Colloids Surf. A 279: 196–207.

Vieira, R.S., E. Guibal, E.A. Silva, and M.M. Beppu. 2007. Adsorption and desorption of binary mixtures of copper and mercury ions on natural and crosslinked chitosan membranes. Adsorption 13: 603–611.

Vikhoreva, G.A. 2012. Processing of chitosan biopolymer into granules, films, and fibers. Fibre Chem. 44: 210–216.

Vimala, K., Y.M. Mohan, K.S. Sivudu, K. Varaprasad, S. Ravindra, N.N. Reddy, Y. Padma, B. Sreedhar, and K. MohanaRaju. 2010. Fabrication of porous chitosan films impregnated with silver nanoparticles: A facile approach for superior antibacterial application. Colloids Surf. B 76: 248–258.

Vincent, C., A. Hertz, T. Vincent, Y. Barré, and E. Guibal. 2014. Immobilization of inorganic ion-exchanger into biopolymer foams—Application to cesium sorption. Chem. Eng. J. 236: 202–211.

Vincent, T. and E. Guibal. 2000. Non-dispersive liquid extraction of Cr(VI) by TBP/Aliquat 336 using chitosan-made hollow fiber. Solv. Extr. Ion Exch. 18: 1241–1260.

Vincent, T. and E. Guibal. 2001. Cr(VI) extraction using Aliquat 336 in a hollow fiber module made of chitosan. Ind. Eng. Chem. Res. 40: 1406–1411.

Vincent, T. and E. Guibal. 2002. Chitosan-supported palladium catalyst. 1. Synthesis procedure. Ind. Eng. Chem. Res. 41: 5158–5164.

Vincent, T. and E. Guibal. 2003. Chitosan-supported palladium catalyst. 3. Influence of experimental parameters on nitrophenol degradation. Langmuir 19: 8475–8483.

Vincent, T. and E. Guibal. 2004. Chitosan-supported palladium catalyst. 5. Nitrophenol degradation using palladium supported on hollow chitosan fibers. Environ. Sci. Technol. 38: 4233–4240.

Vincent, T., P. Krys, C. Jouannin, A.C. Gaumont, I. Dez, and E. Guibal. 2013. Hybrid macroporous Pd catalytic discs for 4-nitroaniline hydrogenation: Contribution of the alginatetetraalkylphosphonium ionic liquid support. J. Organomet. Chem. 723: 90–97.

Vincent, T., S. Spinelli, and E. Guibal. 2003. Chitosan-supported palladium catalyst. II. Chlorophenol dehalogenation. Ind. Eng. Chem. Res. 42: 5968–5976.

Vold, I.M.N., K.M. Varum, E. Guibal, and O. Smidsrod. 2003. Binding of ions to chitosan— Selectivity studies. Carbohydr. Polym. 54: 471–477.

Wang, X., Y.M. Du, and H. Liu. 2004. Preparation, characterization and antimicrobial activity of chitosan—Zn complex. Carbohydr. Polym. 56: 21–26.

Webster, A., M.D. Halling, and D.M. Grant. 2007. Metal complexation of chitosan and its glutaraldehyde cross-linked derivative. Carbohydr. Res. 342: 1189–1201.

Wu, F.C., R.L. Tseng, and R.S. Juang. 1999. Role of pH in metal adsorption from aqueous solutions containing chelating agents on chitosan. Ind. Eng. Chem. Res. 38: 270–275.

Wu, J., M. Luan, and J. Zhao. 2006. Trypsin immobilization by direct adsorption on metal ion chelated macroporous chitosan-silica gel beads. Int. J. Biol. Macromol. 39: 185–191.

Wu, S.-J., T.-H. Liou, C.-H. Yeh, F.-L. Mi, and T.-K. Lin. 2013. Preparation and characterization of porous chitosan-tripolyphosphate beads for copper(II) ion adsorption. J. Appl. Polym. Sci. 127: 4573–4580.

Wu, Y., H. Mimura, and Y. Niibori. 2009. Selective uptake of plutonium (IV) on calcium alginate gel polymer and TBP microcapsule. J. Radioanal. Nucl. Chem. 281: 513–520.

Yamani, J.S., S.M. Miller, M.L. Spaulding, and J.B. Zimmerman. 2012. Enhanced arsenic removal using mixed metal oxide impregnated chitosan beads. Water Res. 46: 4427–4434.

Yang, J., J.-H. Yu, J.R. Strickler, W.-J. Chang, and S. Gunasekaran. 2013. Nickel nanoparticlechitosan-reduced graphene oxide-modi�ed screen-printed electrodes for enzyme-free glucose sensing in portable micro�uidic devices. Biosens. Bioelectron. 47: 530–538.

Yang, J.-S., Y.-J. Xie, and W. He. 2011. Research progress on chemical modification of alginate: A review. Carbohydr. Polym. 84: 33–39.

Ye, X.S., Z.J. Wu, W. Li, H.N. Liu, Q. Li, B.J. Qing, M. Guo, and F. Go. 2009. Rubidium and cesium ion adsorption by an ammonium molybdophosphate-calcium alginate composite adsorbent. Colloids Surf. A 342: 76–83.

Yipmantin, A., H.J. Maldonado, M. Ly, J.M. Taulemesse, and E. Guibal. 2011. Pb(II) and Cd(II) biosorption on Chondracanthus chamissoi (a red alga). J. Hazard. Mater. 185: 922–929.

Yoshizuka, K., Z.R. Lou, and K. Inoue. 2000. Silver-complexed chitosan microparticles for pesticide removal. React. Funct. Polym. 44: 47–54.

Zhang, M., Y. Song, L. Wang, L. Wan, X. Xiao, and S. Ye. 2012. Novel hydrogen peroxide sensor based on chitosan-Ag nanoparticles electrodeposited on glassy carbon electrode. Asian J. Chem. 24: 18–22.

Zhou, L., J. Xu, X. Liang, and Z. Liu. 2010. Adsorption of platinum(IV) and palladium(II) from aqueous solution by magnetic cross-linking chitosan nanoparticles modified with ethylenediamine. J. Hazard. Mater. 182: 518–524.

10 Chapter 10: Mixed-Mode Sorbents in Solid-Phase Extraction

Abdel-Hamid, M., L. Sharaf, S. Kombian, and F. Diejomaoh. 2006. Determination of dydrogesterone in human plasma by tandem mass spectrometry: Application to therapeutic drug monitoring of dydrogesterone in gynecological disorders. Chromatographia 64: 287–292.

Allanson, A.L., M.M. Cotton, J.N.A. Tettey, and A.C. Boyter. 2007. Determination of rifampicin in human plasma and blood spots by high performance liquid chromatography with UV detection: A potential method for therapeutic drug monitoring. J. Pharm. Biomed. Anal. 44: 963–969.

Anthemidis, A.N., S. Xidia, and G. Giakisikli. 2012. Study of bond Elut ® Plexa™ PCX cation exchange resin in flow injection column preconcentration system for metal determination by flame atomic absorption spectrometry. Talanta 97: 181–186.

Batt, A.L., M.S. Kostich, and J.M. Lazorchak. 2008. Analysis of ecologically relevant pharmaceuticals in wastewater and surface water using selective solid-phase extraction and UPLC&MS/MS. Anal. Chem. 80: 5021–5030.

Benito-Peña, E., A.I. Partal-Rodera, M.E. León-González, and M.C. Moreno-Bondi. 2006. Evaluation of mixed mode solid phase extraction cartridges for the preconcentration of beta-lactam antibiotics in wastewater using liquid chromatography with UV-DAD detection. Anal. Chim. Acta 556: 415–422.

Berg, T., E. Lundanes, A.S. Christophersen, and D.H. Strand. 2009. Determination of opiates and cocaine in urine by high pH mobile phase reversed phase UPLC-MS/MS. J. Chromatogr. B 877: 421–432.

Bermudo, E., E. Moyano, L. Puignou, and M.T. Galceran. 2006. Determination of acrylamide in foodstuffs by liquid chromatography ion-trap tandem mass-spectrometry using an improved clean-up procedure. Anal. Chim. Acta 559: 207–214.

Bijlsma, L., J.V. Sancho, E. Pitarch, M. Ibáñez, and F. Hernández. 2009. Simultaneous ultrahigh-pressure liquid chromatography-tandem mass spectrometry determination of amphetamine and amphetamine-like stimulants, cocaine and its metabolites, and a cannabis metabolite in surface water and urban wastewater. J. Chromatogr. A 1216: 3078–3089.

Bratkowska, D., A. Davies, N. Fontanals, P.A.G. Cormack, F. Borrull, D.C. Sherrington, and R.M. Marcé. 2012a. Hypercrosslinked strong anion-exchange resin for extraction of acidic pharmaceuticals from environmental water. J. Sep. Sci. 35: 2621–2628.

Bratkowska, D., N. Fontanals, S. Ronka, F. Borrull, A.W. Trochimczuk, and R.M. Marcé. 2012b. Comparison of different imidazolium supported ionic liquid polymeric phases with strong anion-exchange character for the extraction of acidic pharmaceuticals from complex environmental samples. J. Sep. Sci. 35: 1953–1958.

Bratkowska, D., R.M. Marcé, P.A.G. Cormack, D.C. Sherrington, F. Borrull, and N. Fontanals. 2010. Synthesis and application of hypercrosslinked polymers with weak cationexchange character for the selective extraction of basic pharmaceuticals from complex environmental water samples. J. Chromatogr. A 1217: 1575–1582.

Brousmiche, D.W., J.E. O'Gara, D.P. Walsh, P.J. Lee, P.C. Iraneta, B.C. Trammell, Y. Xu, and C.R. Mallet. 2008. Functionalization of divinylbenzene/N-vinylpyrrolidone copolymer particles: Ion exchangers for solid phase extraction. J. Chromatogr. A 1191: 108–117.

Carli, D., M. Honorat, S. Cohen, M. Megherbi, B. Vignal, C. Dumontet, L. Payen, and J. Guitton. 2009. Simultaneous quantification of 5-FU, 5-FUrd, 5-FdUrd, 5-FdUMP, dUMP and TMP in cultured cell models by LC-MS/MS. J. Chromatogr. B 877: 2937–2944.

Carpinteiro, I., M. Ramil, I. Rodríguez, and R. Cela. 2010. Determination of fungicides in wine by mixed-mode solid phase extraction and liquid chromatography coupled to tandem mass spectrometry. J. Chromatogr. A 1217: 7484–7492.

Chen, H.-C. and W.-H. Ding. 2006. Hot-water and solid-phase extraction of fluorescent whitening agents in paper materials and infant clothes followed by unequivocal determination with ion-pair chromatography-tandem mass spectrometry. J. Chromatogr. A 1108: 202–207.

Chen, H.-C., S.-P. Wang, and W.-H. Ding. 2006. Determination of fluorescent whitening agents in environmental waters by solid-phase extraction and ion pair liquid chromatographytandem mass spectrometry. J. Chromatogr. A 1102: 135–142.

Chiuminatto, U., F. Gosetti, P. Dossetto, E. Mazzucco, D.

Zampieri, E. Robotti, M.C. Gennaro, and E. Marengo. 2010. Automated online solid phase extraction ultra high performance liquid chromatography method coupled with tandem mass spectrometry for determination of forty-two therapeutic drugs and drugs of abuse in human urine. Anal. Chem. 82: 5636–5645.

Clark, Z.D. and E.L. Frank. 2011. Urinary metanephrines by liquid chromatography tandem mass spectrometry: Using multiple quantification methods to minimize interferences in a high throughput method. J. Chromatogr. B 879: 3673–3680.

Coles, R. and E.D. Kharasch. 2007. Stereoselective analysis of bupropion and hydroxybupropion in human plasma and urine by LC/MS/MS. J. Chromatogr. B 857: 67–75.

Cormack, P.A.G., A. Davies, and N. Fontanals. 2012. Synthesis and characterisation of microporous polymers microspheres with strong-cation exchange character. React. Funct. Polym. 72: 939–946.

Culleré, L., M. Bueno, J. Cacho, and V. Ferreira. 2010. Selectivity and efficiency of different reversed-phase and mixed-mode sorbents to preconcentrate and isolate aroma molecules. J. Chromatogr. A 1217: 1557–1566.

Cunliffe, J.M., C.F. Noren, R.N. Hayes, R.P. Clement, and J.X. Shen. 2009. A high-throughput LC-MS/MS method for the quantitation of posaconazole in human plasma: Implementing fused core silica liquid chromatography. J. Pharm. Biomed. Anal. 50: 46–52.

de Jong, W.H.A., K.S. Graham, J.C. van der Molen, T.P. Links, M.R. Morris, H.A. Ross, E.G.E. de Vries, and I.P. Kema. 2007. Plasma free metanephrine measurement using automated online solid-phase extraction HPLC-tandem mass spectrometry. Clin. Chem. 53: 1684–1693.

Díaz-Cruz, M.S., M.J. García-Galán, and D. Barceló. 2008. Highly sensitive simultaneous determination of sulfonamide antibiotics and one metabolite in environmental waters by liquid chromatography-quadrupole linear ion trap-mass spectrometry. J. Chromatogr. A 1193: 50–59.

Dowling, G. and L. Regan. 2011. A new mixed-mode solid phase extraction strategy for opioids, cocaines, amphetamines and adulterants in human blood with hybrid liquid chromatography tandem mass spectrometry detection. J. Pharm. Biomed. Anal. 54: 1136–1145.

Emotte, C., O. Heudi, F. Deglave, A. Bonvie, L. Masson, F. Picard, A. Chaturvedi et al. 2012. Validation of an on-line solid-phase extraction method coupled to liquid chromatographytandem mass spectrometry detection for the determination of Indacaterol in human serum. J. Chromatogr. B 895–896: 1–9.

Fauvelle, V., N. Mazzella, F. Delmas, K. Madarassou, M. Eon, and H. Budzinski. 2012. Use of mixed-mode ion exchange sorbent for the passive sampling of organic acids by polar organic chemical integrative sampler (POCIS). Environ. Sci. Technol. 46: 13344–13353.

Fontanals, N., F. Borrull, and R.M. Marcé. 2013. On-line weak cationic mixed-mode solidphase extraction coupled to liquid chromatography–mass spectrometry to determine illicit drugs at low concentration levels from environmental waters. J. Chromatogr. A 1286: 16–21.

Fontanals, N., P.A.G. Cormack, R.M. Marcé, and F. Borrull. 2010a. Mixed-mode ion-exchange polymeric sorbents: Dual-phase materials that improve selectivity and capacity. Trends Anal. Chem. 29: 765–779.

Fontanals, N., P.A.G. Cormack, and D.C. Sherrington. 2008. Hypercrosslinked polymer microspheres with weak anion-exchange character. Preparation of the microspheres and their applications in pH-tuneable, selective extractions of analytes from complex environmental samples. J. Chromatogr. A 1215: 21–29.

Fontanals, N., P.A.G. Cormack, D.C. Sherrington, R.M. Marcé, and F. Borrull. 2010b. Weakanion exchange hypercrosslinked sorbent in on-line solid-phase extraction-liquid chromatography coupling to achieve automated determination with an effective clean-up. J. Chromatogr. A 1217: 2855–2861.

Fontanals, N., R.M. Marcé, and F. Borrull. 2007. New materials in sorptive extraction techniques for polar compounds. J. Chromatogr. A 1152: 14–31.

Fontanals, N., S. Ronka, F. Borrull, A.T. Trochimczuk, and R.M. Marcé. 2009. Supported imidazolium ionic liquid phases: A new material for solid-phase extraction. Talanta 80: 250–256.

Fontanals, N., B.C. Trammell, M. Galià, R.M. Marcé, P.C. Iraneta, F. Borrull, and U.D. Neue. 2006. Comparison of mixed-mode anion-exchange performance of

N-vinylimidazoledivinylbenzene sorbent. J. Sep. Sci. 29: 1622–1629.

Fountain, K.J., Z. Yin, and D.M. Diehl. 2009. Simultaneous analysis of morphine-related compounds in plasma using mixed-mode solid phase extraction and UltraPerformance liquid chromatography-mass spectrometry. J. Sep. Sci. 32: 2319–2326.

García-López, M., I. Rodríguez, and R. Cela. 2010. Mixed-mode solid-phase extraction followed by liquid chromatography-tandem mass spectrometry for the determination of tri- and di-substituted organophosphorus species in water samples. J. Chromatogr. A 1217: 1476–1484.

Ge, L., C.Y.C. Peh, J.W.H. Yong, S.N. Tan, L. Hua, and E.S. Ong. 2007. Analyses of gibberellins by capillary electrophoresis-mass spectrometry combined with solid-phase extraction. J. Chromatogr. A 1159: 242–249.

Ge, L., J.W.H. Yong, S.N. Tan, X.H. Yang, and E.S. Ong. 2006. Analysis of cytokinin nucleotides in coconut (Cocos nucifera L.) water using capillary zone electrophoresis-tandem mass spectrometry after solid-phase extraction. J. Chromatogr. A 1133: 322–331.

Gheorghe, A., A. van Nuijs, B. Pecceu, L. Bervoets, P. Jorens, R. Blust, H. Neels, and A. Covaci. 2008. Analysis of cocaine and its principal metabolites in waste and surface water using solid-phase extraction and liquid chromatography-ion trap tandem mass spectrometry. Anal. Bioanal. Chem. 391: 1309–1319.

Gil-Garcia, M.D., M.J. Culzoni, M.M. De Zan, R. Santiago-Valverde, M. Martínez-Galera, and H.C. Goicoechea. 2008. Solving matrix effects exploiting the second-order advantage in the resolution and determination of eight tetracycline antibiotics in effluent wastewater by modelling liquid chromatography data with multivariate curve resolution-alternating least squares and unfolded-partial least squares followed by residual bilinearization algorithms: II. Prediction and figures of merit. J. Chromatogr. A 1179: 115–124.

Gilart, N., R.M. Marcé, F. Borrull, and N. Fontanals. 2012. Determination of pharmaceuticals in wastewaters using solid-phase extraction-liquid chromatography-tandem mass spectrometry. J. Sep. Sci. 35: 875–882.

González-Mariño, I., J.B. Quintana, I. Rodríguez, M. González-Díez, and R. Cela. 2011. Screening and selective quantification of illicit drugs in wastewater by mixed-mode solid-phase extraction and quadrupole-time-of-flight liquid chromatography–mass spectrometry. Anal. Chem. 84: 1708–1717.

Gros, M., M. Petrovic, and D. Barceló. 2006. Development of a multi-residue analytical methodology based on liquid chromatography–tandem mass spectrometry (LC-MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters. Talanta 70: 678–690.

Gros, M., M. Petrovic, and D. Barceló. 2009. Tracing pharmaceutical residues of different therapeutic classes in environmental waters by using liquid chromatography/quadrupolelinear ion trap mass spectrometry and automated library searching. Anal. Chem. 81: 898–912.

Harris, S.R., J.I. Gedge, A.N.R. Nedderman, S.J. Roffey, and M. Savage. 2004. A sensitive HPLC-MS-MS assay for quantitative determination of midazolam in dog plasma. J. Pharm. Biomed. Anal. 35: 127–134.

Heinig, K. and T. Wirz. 2009. Determination of taspoglutide in human and animal plasma using liquid chromatography-tandem mass spectrometry with orthogonal columnswitching. Anal. Chem. 81: 3705–3713.

Hewitt, D., M. Alvarez, K. Robinson, J. Ji, Y.J. Wang, Y.H. Kao, and T. Zhang. 2011. Mixedmode and reversed-phase liquid chromatography-tandem mass spectrometry methodologies to study composition and base hydrolysis of polysorbate 20 and 80. J. Chromatogr. A 1218: 2138–2145.

Huq, S., M. Garriques, and K.M.R. Kallury. 2006. Role of zwitterionic structures in the solidphase extraction based method development for clean up of tetracycline and oxytetracycline from honey. J. Chromatogr. A 1135: 12–18.

Ivanov Dobrev, P. and M. Kaminek. 2002. Fast and efficient separation of cytokinins from auxin and abscisic acid and their purification using mixed-mode solid-phase extraction. J. Chromatogr. A 950: 21–29.

Izumi, Y., A. Okazawa, T. Bamba, A. Kobayashi, and E. Fukusaki. 2009. Development of a method for comprehensive and quantitative analysis of plant hormones by highly sensitive nanoflow liquid chromatography-electrospray ionization-ion trap mass spectrometry. Anal. Chim. Acta

648: 215–225.

Johansen, K.T., S.J. Ebild, S.B. Christensen, M. Godejohann, and J.W. Jaroszewski. 2012. Alkaloid analysis by high-performance liquid chromatography-solid phase extractionnuclear magnetic resonance: New strategies going beyond the standard. J. Chromatogr. A 1270: 171–177.

Josefsson, M. and A. Sabanovic. 2006. Sample preparation on polymeric solid phase extraction sorbents for liquid chromatographic-tandem mass spectrometric analysis of human whole blood—A study on a number of beta-agonists and beta-antagonists. J. Chromatogr. A 1120: 1–12.

Kakimoto, K., A. Toriba, T. Ohno, M. Ueno, T. Kameda, N. Tang, and K. Hayakawa. 2008. Direct measurement of the glucuronide conjugate of 1-hydroxypyrene in human urine by using liquid chromatography with tandem mass spectrometry. J. Chromatogr. B 867: 259–263.

Kanaujia, P.K., D. Pardasani, A.K. Purohit, V. Tak, and D.K. Dubey. 2011. Polyelectrolyte functionalized multi-walled carbon nanotubes as strong anion-exchange material for the extraction of acidic degradation products of nerve agents. J. Chromatogr. A 1218: 9307–9313.

Karlonas, N., A. Padarauskas, A. Ramanavicius, and A. Ramanaviciene. 2013. Mixed-mode SPE for a multi-residue analysis of benzodiazepines in whole blood using rapid GC with negative-ion chemical ionization MS. J. Sep. Sci. 36: 1437–1445.

Kaserzon, S.L., K. Kennedy, D.W. Hawker, J. Thompson, S. Carter, A.C. Roach, K. Booij, and J.F. Mueller. 2012. Development and calibration of a passive sampler for per�uorinated alkyl carboxylates and sulfonates in water. Environ. Sci. Technol. 46: 4985–4993.

Kasprzyk-Hordern, B., R.M. Dinsdale, and A.J. Guwy. 2007. Multi-residue method for the determination of basic/neutral pharmaceuticals and illicit drugs in surface water by solid-phase extraction and ultra performance liquid chromatography-positive electrospray ionisation tandem mass spectrometry. J. Chromatogr. A 1161: 132–145.

Kharbouche, H., F. Sporkert, S. Troxler, M. Augsburger, P. Mangin, and C. Staub. 2009. Development and validation of a gas chromatography-negative chemical ionization tandem mass spectrometry method for the determination of ethyl glucuronide in hair and its application to forensic toxicology. J. Chromatogr. B 877: 2337–2343.

Kirchner, B. 2009. Ionic Liquids. Springer, Berlin, Germany.

Klinke, H.B. and K. Linnet. 2007. Performance of four mixed-mode solid-phase extraction columns applied to basic drugs in urine. Scand. J. Clin. Lab. Invest. 67: 778–782.

Kojima, M., S. Tsunoi, and M. Tanaka. 2004. High performance solid-phase analytical derivatization of phenols for gas chromatography-mass spectrometry. J. Chromatogr. A 1042: 1–7.

Kollroser, M. and C. Schober. 2002. Determination of amiodarone and desethylamiodarone in human plasma by high-performance liquid chromatography-electrospray ionization tandem mass spectrometry with an ion trap detector. J. Chromatogr. B 766: 219–226.

Kusch, P., G. Knupp, M. Hergarten, M. Kozupa, and M. Majchrzak. 2006. Solid-phase extraction-gas chromatography and solid-phase extraction-gas chromatographymass spectrometry determination of corrosion inhibiting long-chain primary alkyl amines in chemical treatment of boiler water in water-steam systems of power plants. J. Chromatogr. A 1113: 198–205.

Lai, S.S.L., H.S. Yeung, W.O. Lee, C. Ho, and Y.T. Wong. 2011. Determination of closantel and rafoxanide in animal tissues by online anionic mixed-mode solid-phase extraction followed by isotope dilution liquid chromatography tandem mass spectrometry. J. Sep. Sci. 34: 1366–1374.

Landberg, R., P. Aman, and A. Kamal-Eldin. 2009. A rapid gas chromatography-mass spectrometry method for quantification of alkylresorcinols in human plasma. Anal. Biochem. 385: 7–12.

Lara, F.J., A.M. García-Campaña, F. Ales-Barrero, J.M. Bosque-Sendra, and L.E. GarcíaAyuso. 2006. Multiresidue method for the determination of quinolone antibiotics in bovine raw milk by capillary electrophoresis-tandem mass spectrometry. Anal. Chem. 78: 7665–7673.

Lavén, M., T. Alsberg, Y. Yu, M. Adolfsson-Erici, and H. Sun. 2009. Serial mixed-mode cation- and anion-exchange solid-phase extraction for separation of basic, neutral and acidic pharmaceuticals in wastewater and analysis by high-performance liquid chromatography-quadrupole time-of-flight mass spectrometry. J. Chromatogr. A 1216:

49–62.

Lee, H.-B., T.E. Peart, and M.L. Svoboda. 2007. Determination of ofloxacin, norfloxacin, and ciprofloxacin in sewage by selective solid-phase extraction, liquid chromatography with fluorescence detection, and liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1139: 45–52.

Lehtonen, P., H. Siren, I. Ojanpera, and R. Kostiainen. 2004. Migration behaviour and separation of tramadol metabolites and diastereomeric separation of tramadol glucuronides by capillary electrophoresis. J. Chromatogr. A 1041: 227–234.

Li, K., H. Wang, C.O. Brant, S. Ahn, and W. Li. 2011. Multiplex quantification of lamprey specific bile acid derivatives in environmental water using UHPLC-MS/MS. J. Chromatogr. B 879: 3879–3886.

Li, Y., A.C. Li, H. Shi, H. Junga, X. Jiang, W. Naidong, and J.H. Lauterbach. 2006. Determination of S-phenylmercapturic acid in human urine using an automated sample extraction and fast liquid chromatography-tandem mass spectrometric method. Biomed. Chromatogr. 20: 597–604.

Lin, Z.J., S.-X. Qiu, A. Wufuer, and L. Shum. 2005. Simultaneous determination of glycyrrhizin, a marker component in radix Glycyrrhizae, and its major metabolite glycyrrhetic acid in human plasma by LC-MS/MS. J. Chromatogr. B 814: 201–207.

Lõpez, R., E. Gracia-Moreno, J. Cacho, and V. Ferrreira. 2011. Development of a mixed-mode solid phase extraction method and further gas chromatography mass spectrometry for the analysis of 3-alkyl-2-methoxypyrazines in wine. J. Chromatogr. A 1218: 842–848.

Luque, N. and S. Rubio. 2012. Extraction and stability of pesticide multiresidues from natural water on a mixed-mode admicellar sorbent. J. Chromatogr. A 1248: 74–83.

Malakova, J., M. Nobilis, Z. Svoboda, M. Lisa, M. Holcapek, J. Kvetina, J. Klimes, and V. Palicka. 2007. High-performance liquid chromatographic method with UV photodiode-array, fluorescence and mass spectrometric detection for simultaneous determination of galantamine and its phase I metabolites in biological samples. J. Chromatogr. B 853: 265–274.

Marchi, I., S. Rudaz, and J.-L. Veuthey. 2009. Sample preparation development and matrix effects evaluation for multianalyte determination in urine. J. Pharm. Biomed. Anal. 49: 459–467.

Martín-Esteban, A. 2013. Molecularly-imprinted polymers as a versatile, highly selective tool in sample preparation. TrAC Trends Anal. Chem. 45: 169–181.

Matejicek, D., P. Houserova, and V. Kuban. 2007. Combined isolation and purification procedures prior to the high-performance liquid chromatographic-ion-trap tandem mass spectrometric determination of estrogens and their conjugates in river sediments. J. Chromatogr. A 1171: 80–89.

Montes, R., M. García-López, I. Rodríguez, and R. Cela. 2010. Mixed-mode solid-phase extraction followed by acetylation and gas chromatography mass spectrometry for the reliable determination of trans-resveratrol in wine samples. Anal. Chim. Acta 673: 47–53.

Msagati, T.A.M. and M.M. Nindi. 2006. Comparative study of sample preparation methods; supported liquid membrane and solid phase extraction in the determination of benzimidazole anthelmintics in biological matrices by liquid chromatography-electrospray-mass spectrometry. Talanta 69: 243–250.

Musenga, A. and D.A. Cowan. 2013. Use of ultra-high pressure liquid chromatography coupled to high resolution mass spectrometry for fast screening in high throughput doping control. J. Chromatogr. A 1288: 82–95.

Nanita, S.C., A.M. Pentz, J. Grant, E. Vogl, T.J. Devine, and R.M. Henze. 2008. Mass spectrometric assessment and analytical methods for quantitation of the new herbicide aminocyclopyrachlor and its methyl analogue in soil and water. Anal. Chem. 81: 797–808.

Nochetto, C.B., R. Reimschuessel, C. Gieseker, C.S. Cheely, and M.C. Carson. 2009. Determination of tricaine residues in fish by liquid chromatography. J. AOAC Int. 92: 1241–1248.

Park, J.W., J.S.J. Hong, N. Parajuli, H.S. Koh, S.R. Park, M.-O. Lee, S.-K. Lim, and Y.J. Yoon. 2007. Analytical profiling of biosynthetic intermediates involved in the gentamicin pathway of Micromonospora echinospora by high-performance liquid chromatography using electrospray ionization mass spectrometric detection. Anal. Chem. 79: 4860–4869.

Pedrouzo, M., F. Borrull, E. Pocurull, and R.M. Marcé. 2011. Drugs of abuse and their metabolites in waste and surface waters by liquid chromatography-tandem mass spectrometry. J. Sep. Sci. 34: 1091–1101.

Peru, K.M., S.L. Kuchta, J.V. Headley, and A.J. Cessna. 2006. Development of hydrophilic interaction chromatography-mass spectrometry assay for spectinomycin and lincomycin in liquid hog manure supernatant and run off from cropland. J. Chromatogr. A 1107: 152–158.

Ramos, L. 2012. Critical overview of selected contemporary sample preparation techniques. J. Chromatogr. A 1221: 84–98.

Ratpukdi, T., J.A. Rice, G. Chilom, A. Bezbaruah, and E. Khan. 2009. Rapid fractionation of natural organic matter in water using a novel solid-phase extraction technique. Water Environ. Res. 81: 2299–2308.

Regueiro, J., E. Martín-Morales, G. Álvarez, and J. Blanco. 2011. Sensitive determination of domoic acid in shellfish by on-line coupling of weak anion exchange solid-phase extraction and liquid chromatography–diode array detection–tandem mass spectrometry. Food Chem. 129: 672–678.

Roberts, P.H. and P. Bersuder. 2006. Analysis of OSPAR priority pharmaceuticals using highperformance liquid chromatography-electrospray ionisation tandem mass spectrometry. J. Chromatogr. A 1134: 143–150.

Rodríguez-Gonzalo, E., R. Carabias-Martínez, E.M. Cruz, J. Domínguez-Álvarez, and J. Hernández-Méndez. 2009. Ultrasonic solvent extraction and nonaqueous CE for the determination of herbicide residues in potatoes. J. Sep. Sci. 32: 575–584.

Schonberg, L., T. Grobosch, D. Lampe, and C. Kloft. 2006. New screening method for basic compounds in urine by on-line extraction-high-performance liquid chromatography with photodiode-array detection. J. Chromatogr. A 1134: 177–185.

Seitz, W., W. Schulz, and W.H. Weber. 2006. Novel applications of highly sensitive liquid chromatography/mass spectrometry/mass spectrometry for the direct detection of ultra-trace levels of contaminants in water. Rapid Commun. Mass Spectrom. 20: 2281–2285.

Sentellas, S., E. Moyano, L. Puignou, and M.T. Galceran. 2004. Optimization of a cleanup procedure for the determination of heterocyclic aromatic amines in urine by eld- ampliﬁed sample injection-capillary electrophoresis-mass spectrometry. J. Chromatogr. A 1032: 193–201.

Shi, Z.-G., F. Chen, J. Xing, and Y.-Q. Feng. 2009. Carbon monolith: Preparation, characterization and application as microextraction ﬁber. J. Chromatogr. A 1216: 5333–5339.

Siwek, M., A. Noubar, R. Erdmann, B. Niemeyer, and B. Galunsky. 2008. Application of mixed-mode oasis MCX adsorbent for chromatographic separation of selenomethionine from antarctic krill after enzymatic digestion. Chromatographia 67: 305–308.

Sousa, M., C. Gonçalves, E. Cunha, J. Hajslová, and M. Alpendurada. 2011. Cleanup strategies and advantages in the determination of several therapeutic classes of pharmaceuticals in wastewater samples by SPE-LC-MS/MS. Anal. Bioanal. Chem. 399: 807–822.

Strahm, E., I. Kohler, S. Rudaz, S. Martel, P.-A. Carrupt, J.-L. Veuthey, M. Saugy, and C. Saudan. 2008a. Isolation and quantiﬁcation by high-performance liquid chromatography-iontrap mass spectrometry of androgen sulfoconjugates in human urine. J. Chromatogr. A 1196–1197: 153–160.

Strahm, E., S. Rudaz, J.-L. Veuthey, M. Saugy, and C. Saudan. 2008b. Proﬁling of 19-norsteroid sulfoconjugates in human urine by liquid chromatography mass spectrometry. Anal. Chim. Acta 613: 228–237.

Sun, H., F. Wang, and L. Ai. 2007. Validated method for determination of ultra-trace closantel residues in bovine tissues and milk by solid-phase extraction and liquid chromatographyelectrospray ionization-tandem mass spectrometry. J. Chromatogr. A 1175: 227–233.

Taniyasu, S., K. Kannan, M.K. So, A. Gulkowska, E. Sinclair, T. Okazawa, and N. Yamashita. 2005. Analysis of uorotelomer alcohols, ﬂuorotelomer acids, and short- and long-chain perﬂuorinated acids in water and biota. J. Chromatogr. A 1093: 89–97.

Tansupo, P., P. Suwannasom, D.L. Luthria, S. Chanthai, and C. Ruangviriyachai. 2010. Optimised separation procedures for the simultaneous assay of three plant hormones in liquid biofertilisers. Phytochem. Anal. 21: 157–162.

Tauxe-Wuersch, A., L.F. De Alencastro, D. Grandjean, and J. Tarradellas. 2006. Trace determination of tamoxifen and 5-fluorouracil in hospital and urban wastewaters. Int. J. Environ. Anal. Chem. 86: 473–485.

Tsyurupa, M.P. and V.A. Davankov. 2002. Hypercrosslinked polymers: Basic principles of preparing the new class of polymeric materials. React. Funct. Polym. 53: 193–203.

Tylová, T., M. Kolařík, and J. Olšovská. 2011. The UHPLC-DAD fingerprinting method for analysis of extracellular metabolites of fungi of the genus Geosmithia (Ascomycota: Hypocreales). Anal. Bioanal. Chem. 400: 2943–2952.

Van De Steene, J.C., K.A. Mortier, and W.E. Lambert. 2006. Tackling matrix effects during development of a liquid chromatographic-electrospray ionisation tandem mass spectrometric analysis of nine basic pharmaceuticals in aqueous environmental samples. J. Chromatogr. A 1123: 71–81.

Vidal, L., M.-L. Riekkola, and A. Canals. 2012. Ionic liquid-modified materials for solidphase extraction and separation: A review. Anal. Chim. Acta 715: 19–41.

Wang, Z., Z. Wang, J. Wen, and Y. He. 2007. Simultaneous determination of three aconitum alkaloids in urine by LC-MS-MS. J. Pharm. Biomed. Anal. 45: 145–148.

Weigel, S., R. Kallenborn, and H. Hühnerfuss. 2004. Simultaneous solid-phase extraction of acidic, neutral and basic pharmaceuticals from aqueous samples at ambient (neutral) pH and their determination by gas chromatography-mass spectrometry. J. Chromatogr. A 1023: 183–195.

Williams, L. and J. Caulfield. 2009. High throughput extraction of melanin using Evolute CX mixed-mode SPE plates. LC·GC North America Feb, pp. 44–47.

Wu, X., B. Zhu, L. Lu, W. Huang, and D. Pang. 2012. Optimization of a solid phase extraction and hydrophilic interaction liquid chromatography-tandem mass spectrometry method for the determination of metformin in dietary supplements and herbal medicines. Food Chem. 133: 482–488.

Wu, Y.Y., W.X. Shi, and S.Q. Chen. 2009. Determination of beta-estradiol, bisphenol A, diethylstilbestrol and salbutamol in human urine by GC/MS. Zhejiang Da Xue Xue Bao Yi Xue Ban 38: 235–241.

Xia, X., X. Li, S. Ding, S. Zhang, H. Jiang, J. Li, and J. Shen. 2009. Ultra-high-pressure liquid chromatography-tandem mass spectrometry for the analysis of six resorcylic acid lactones in bovine milk. J. Chromatogr. A 1216: 2587–2591.

Xu, Y., L. Du, E.D. Soli, M.P. Braun, D.C. Dean, and D.G. Musson. 2005. Simultaneous determination of a novel KDR kinase inhibitor and its N-oxide metabolite in human plasma using 96-well solid-phase extraction and liquid chromatography/tandem mass spectrometry. J. Chromatogr. B 817: 287–296.

Xue, Y.-J., J.B. Akinsanya, J. Liu, and S.E. Unger. 2006. A simplified protein precipitation/ mixed-mode cation-exchange solid-phase extraction, followed by high-speed liquid chromatography/mass spectrometry, for the determination of a basic drug in human plasma. Rapid Commun. Mass Spectrom. 20: 2660–2668.

Yang, S., R.E. Synovec, M.G. Kalyuzhnaya, and M.E. Lidstrom. 2011. Development of a solid phase extraction protocol coupled with liquid chromatography mass spectrometry to analyze central carbon metabolites in lake sediment microcosms. J. Sep. Sci. 34: 3597–3605.

Yeung, H.-S., W.-O. Lee, and Y.-T. Wong. 2010. Screening of closantel and rafoxanide in animal muscles by HPLC with uorescence detection and confirmation using MS. J. Sep. Sci. 33: 206–211.

Zedda, M., J. Tuerk, S. Peil, and T.C. Schmidt. 2010. Determination of polymer electrolyte membrane (PEM) degradation products in fuel cell water using electrospray ionization tandem mass spectrometry. Rapid Commun. Mass Spectrom. 24: 3531–3538.

Zhao, M., M.A. Rudek, P. He, C. Hartke, S. Gore, M.A. Carducci, and S.D. Baker. 2004. Quantification of 5-azacytidine in plasma by electrospray tandem mass spectrometry coupled with high-performance liquid chromatography. J. Chromatogr. B 813: 81–88.

Zheng, H., L.-G. Deng, X. Lu, S.-C. Zhao, C.-Y. Guo, J.-S. Mao, Y.-T. Wang, G.-S. Yang, and H. Aboul-Enein. 2010. UPLC-ESI-MS-MS determination of three β2-agonists in pork. Chromatographia 72: 79–84.

Zheng, M.M., G.D. Ruan, and Y.Q. Feng. 2009. Hybrid organic-inorganic silica monolith with hydrophobic/strong cation-exchange functional groups as a sorbent for micro-solid phase extraction. J. Chromatogr. A 1216: 7739–7746.

Zhou, J.-L., J.-J. An, P. Li, H.-J. Li, Y. Jiang, and J.-F. Cheng. 2009. Two-dimensional turbulent flow chromatography coupled on-line to liquid chromatography-mass spectrometry for solution-based ligand screening against multiple proteins. J. Chromatogr. A 1216: 2394–2403.

Zhu, L., Y. Deng, J. Zhang, and J. Chen. 2011. Adsorption of phenol from water by N-butylimidazolium functionalized strongly basic anion exchange resin. J. Colloid Interface Sci. 364: 462–468.

Zorita, S., L. Larsson, and L. Mathiasson. 2008. Comparison of solid-phase sorbents for determination of fluoroquinolone antibiotics in wastewater. J. Sep. Sci. 31: 3117–3121.

11 Chapter 11: Interpenetrating Polymer Network Composite Hydrogels and Their Applications in Separation Processes

Agostino, A.D., A. La Gatta, T. Busico, M. De Rosa, and C. Schiraldi. 2012. Semiinterpenetrated hydrogels composed of PVA and hyaluronan or chondroitin sulphate: Chemico-physical and biological characterization. J. Biotechnol. Biomater. 2: Art. 140.

Ajiro, H., Y. Takemoto, T. Asoh, and M. Akashi. 2009. Novel polyion complex with interpenetrating polymer network of poly(acrylic acid) and partially protected poly(vinylamine) using N-vinylacetamide and N-vinylformamide. Polymer 50: 3503–3507.

Alvarez-Lorenzo, C., A. Concheiro, A.S. Dubovik, N.V. Grinberg, T.V. Burova, and V.Y. Grinberg. 2005. Temperature-sensitive chitosan-poly(N-isopropylacrylamide) interpenetrated networks with enhanced loading capacity and controlled release properties. J. Control. Release 102: 629–641.

Amnuaypanich, S. and N. Kongchana. 2009. Natural rubber/poly(acrylic acid) semiinterpenetrating polymer network membranes for the pervaporation of water-ethanol mixtures. J. Appl. Polym. Sci. 114: 3501–3509.

Amnuaypanich, S., J. Patthana, and P. Phinyocheep. 2009. Mixed matrix membranes prepared from natural rubber/poly(vinyl alcohol) semi-interpenetrating polymer network (NR/PVA semi-IPN) incorporating with zeolite 4A for the pervaporation dehydration of water-ethanol mixtures. Chem. Eng. Sci. 64: 4908–4918.

Apopei, D.F., M.V. Dinu, A. Trochimczuk, and E.S. Dragan. 2012. Sorption isotherms of heavy metal ions onto semi-IPN cryogels based on polyacrylamide and anionically modified potato starch. Ind. Eng. Chem. Res. 51: 10462–10471.

Apopei, D.F. and E.S. Dragan. 2013. Semi-interpenetrating polymer networks based on polyacrylamide and starch or modified starch. J. Nanostruct. Polym. Nanocomposites 9: 16–20.

Bajpai, A.K. and A. Mishra. 2004. Ionizable interpenetrating polymer networks of carboxymethyl cellulose and polyacrylic acid: Evaluation of water uptake. J. Appl. Polym. Sci. 93: 2054–2065.

Bajpai, A.K. and A. Mishra. 2005. Preparation and characterization of tetracycline-loaded interpenetrating polymer networks of carboxymethyl cellulose and poly(acrylic acid): Water sorption and drug release study. Polym. Int. 54: 1347–1356.

Baskan, T., D.C. Tuncaboylu, and O. Okay. 2013. Tough interpenetrating Pluronic F127/polyacrylic acid hydrolysis. Polymer 54: 2979–2987.

Baydemir, G., N. Bereli, M. Andac, R. Say, I.Y. Galaev, and A. Denizli. 2009. Bilirubin recognition via molecularly imprinted supermacroporous cryogels. Colloids Surf. B 68: 33–38.

Bessbousse, H., T. Rhlalou, J.-F. Verchere, and L. Lebrun. 2008. Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethyleneimine) in a poly(vinyl alcohol) matrix. J. Membr. Sci. 307: 249–259.

Bessbousse, H., J.-F. Verchere, and L. Lebrun. 2012. Characterisation of metal-complexing membranes prepared by the semi-interpenetrating polymer networks technique. Application to the removal of heavy metal ions from aqueous solutions. Chem. Eng. J. 187: 16–28.

Bhattacharyya, R. and S.K. Ray. 2013. Kinetic and equilibrium modeling for adsorption of textile dyes in aqueous solutions by carboxymethyl cellulose/poly(acrylamide-cohydroxyethyl methacrylate) semi-interpenetrating network hydrogel. Polym. Eng. Sci. 53: 2439–2453.

Bhuniya, S.P., S. Rahman, A.J. Satyanand, M.M. Gharia, and A.M. Dave. 2003. Novel route to synthesis of allyl starch and biodegradable hydrogel by copolymerizing allyl modified starch with methacrylic acid and acrylamide. J. Polym. Sci. Part A: Polym. Chem. 41: 1650–1658.

Bocourt, M., W. Arguelles-Monal, J.V. Cauich-Rodríguez, A. May, N. Bada, and C. Peniche. 2011. Interpenetrated chitosan-poly(acrylic acid-co-acrylamide) hydrogels. Synthesis, characterization and sustained protein release studies. Mater. Sci. Appl. 2: 509–520.

Bonina, P., Ts. Petrova, and N. Manolova. 2004. pH-Sensitive hydrogels composed of chitosan and polyacrylamide—Preparation and properties. J. Bioact. Compat. Polym. 19: 101–116.

Buyanov, A.L., L.G. Revel'skaya, E.Y. Rosova, and G.K. Elyashevich. 2004. Swelling behavior and pervaporation properties of new composite membrane systems: Porous polyethylene film-poly(acrylic acid) hydrogel. J. Appl. Polym. Sci. 94: 1461–1465.

Chauhan, G.S., S. Kumar, A. Kumari, and R. Sharma. 2003. Study on the synthesis, characterization, and sorption of some metal ions on gelatin- and acrylamide-based hydrogels. J. Appl. Polym. Sci. 90: 3856–3871.

Chauhan, G.S. and S. Mahajan. 2002. Use of novel hydrogels based on modified cellulosics and methacrylamide for separation of metal ions from water systems. J. Appl. Polym. Sci. 86: 667–671.

Chauhan, K., G.S. Chauhan, and J.-H. Ahn. 2009. Synthesis and characterization of novel guar gum hydrogels and their use as Cu 2+ sorbents. Bioresour. Technol. 100: 3599–3603.

Chen, J., M. Liu, and S. Chen. 2009. Synthesis and characterization of thermo- and pHsensitive kappa-carrageenan-g-poly(methacrylic acid)/poly(N,N-diethylacrylamide) semi-IPN hydrogel. Mater. Chem. Phys. 115: 339–346.

Chen, J., M. Liu, H. Liu, L. Ma, C. Gao, S. Zhu, and S. Zhang. 2010. Synthesis and properties of thermo- and pH-sensitive poly(diallyldimethylammonium chloride)/ poly(N,N-diethylacrylamide) semi-IPN hydrogel. Chem. Eng. J. 159:247–256.

Chen, S., M. Liu, S. Jin, and Y. Chen. 2005. Synthesis and swelling properties of pH-sensitive hydrogels based on chitosan and poly(methacrylic acid) semi-interpenetrating polymer network. J. Appl. Polym. Sci. 98: 1720–1726.

Crini, G. and P.M. Badot. 2008. Application of chitosan, a natural aminopolysaccharide for dye removal from aqueous solution by adsorption process using batch studies: A review of recent literature. Prog. Polym. Sci. 33: 399–447.

Dalaran, M., S. Emik, G. Guclu, T.B. Iyim, and S. Ozgumus. 2011. Study on a novel polyampholyte nanocomposite superabsorbent hydrogels: Synthesis, characterization and investigation of removal of indigo carmine from aqueous solution. Desalination 279: 170–182.

Demirel, G., G. Özcetin, F. Şahin, H. Tümtürk, S. Aksoy, and N. Hasirci. 2006. Semiinterpenetrating polymer networks (IPNs) for entrapment of glucose isomerase. React. Funct. Polym. 66: 389–394.

Dinu, M.V., M. Cazacu, and E.S. Drăgan. 2013. Mechanical, thermal, and surface properties of poly(acrylamide)/dextran semi-interpenetrating network hydrogels tuned by the synthesis temperature. Cent. Eur. J. Chem. 11: 248–258.

Dinu, M.V., M.M. Ozmen, E.S. Dragan, and O. Okay. 2007. Freezing as a path to build macroporous structures: Superfast responsive polyacrylamide hydrogels. Polymer 48: 195–204.

Dinu, M.V., M.M. Perju, M. Cazacu, and E.S. Drăgan. 2011a. Polyacrylamide-dextran polymeric networks: Effect of gel preparation temperature on their morphology and swelling properties. Cellulose Chem. Technol. 45: 197–203.

Dinu, M.V., M.M. Perju, and E.S. Drăgan. 2011b. Porous semi-interpenetrating hydrogel networks based on dextran and polyacrylamide with superfast responsiveness. Macromol. Chem. Phys. 212: 240–251.

Dinu, M.V., M.M. Perju, and E.S. Drăgan. 2011c. Composite IPN ionic hydrogels based on polyacrylamide and dextran sulfate. React. Funct. Polym. 71: 881–890.

Dinu, M.V., S. Schwarz, I.A. Dinu, and E.S. Drăgan. 2012. Comparative rheological study of ionics-IPN composite hydrogels based on polyacrylamide and dextran sulfate and of polyacrylamide hydrogels. Colloid Polym. Sci. 290: 1647–1657.

Drăgan, E.S. and D.F. Apopei. 2011. Synthesis and swelling behavior of pH-sensitive semiinterpenetrating polymer network composite hydrogels based on native and modified potatoes starch as potential sorbent for cationic dyes. Chem. Eng. J. 178: 252–263.

Drăgan, E.S. and D.F. Apopei. 2013. Multiresponsive macroporous semi-IPN composite hydrogels based on native or anionically modified potato starch. Carbohydr. Polym. 92: 23–32.

Drăgan, E.S. and D.F. Apopei Loghin. 2013. Enhanced sorption of Methylene Blue from aqueous solutions by semi-IPN composite cryogels with anionically modified potato starch entrapped in PAAm matrix. Chem. Eng. J. 234: 211–222.

Drăgan, E.S. and M.V. Dinu. 2013. Design, synthesis and interaction with Cu 2+ of ice templated composite hydrogels. Res. J. Chem. Environ. 17: 4–10.

Drăgan, E.S., M.V. Dinu, and D.F. Apopei. 2012a. Macroporous anionic interpenetrating polymer networks composite hydrogels and their interaction with Methylene Blue. Int. J. Chem. 1: 548–569.

Drăgan, E.S., M.M. Lazăr, M.V. Dinu, and F. Doroftei. 2012b. Macroporous composite IPN hydrogels based on poly(acrylamide) and chitosan with tuned swelling and sorption of cationic dyes. Chem. Eng. J. 204–206: 198–209.

Drăgan, E.S., M.M. Perju, and M.V. Dinu. 2012c. Preparation and characterization of IPN composite hydrogels based on polyacrylamide and chitosan and their interaction with cationic dyes. Carbohydr. Polym. 88: 2270–2281.

Draget, K.I. 2000. Alginates. In Handbook of Hydrocolloids, G.O. Philips and P.A. Williams (eds.). Woodhead Publishing, Cambridge, U.K., pp. 379–395.

Dumitriu, R.P., G.R. Mitchell, and C. Vasile. 2011. Multi-responsive hydrogels based on N-isopropylacrylamide and sodium alginate. Polym. Int. 60: 222–233.

Franson, N.M. and N.A. Peppas. 1983. Influence of copolymer composition on non-Fickian water transport through glassy copolymers. J. Appl. Polym. Sci. 28: 1299–1310.

Freundlich, H.M.F. 1906. Über die adsorption in lösungen. Z. Phys. Chem. 57(A): 385–470.

Gerente, C., V.K.C. Lee, P. Le Cloirec, and G. McKay. 2007. Application of chitosan for the removal of metals from wastewaters by adsorption—Mechanisms and models review. Crit. Rev. Environ. Sci. Technol. 37: 41–127.

Guo, B., J. Yuan, L. Yao, and Q. Gao. 2007. Preparation and release profiles of pH/temperature responsive carboxymethyl chitosan/P(2-(dimethylamino)ethyl methacrylate) semi-IPN amphoteric hydrogel. Colloid Polym. Sci. 285: 665–671.

Hajizadeh, S., H. Kirsebom, I.Y. Galaev, and B. Mattiasson. 2010. Evaluation of selective composite cryogel for bromate removal from drinking water. J. Sep. Sci. 33:

1752–1759.

Hamcerencu, M., J. Desbrieres, A. Khoukh, M. Popa, and G. Riess. 2011. Thermodynamic investigation of thermoresponsive xanthan-poly(N-isopropylacrylamide) hydrogels. Polym. Int. 60: 1527–1534.

Han, Y.A., E.M. Lee, and B.C. Ji. 2008. Mechanical properties of semi-interpenetrating polymer network hydrogels based on poly(2-hydroxyethyl methacrylate) copolymer and chitosan. Fibers Polym. 9: 393–399.

Higa, M., M. Kobayashi, Y. Kakihana, A. Jikihara, and N. Fujiwara. 2013. Charge mosaic membranes with semi-interpenetrating polymer network structures prepared from a polymer blend of poly(vinyl alcohol) and polyelectrolytes. J. Membr. Sci. 428: 267–274.

Ho, Y.S. 2006. Review of second-order models for adsorption systems. J. Hazard. Mater. 136: 681–689.

Ho, Y.S. and G. McKay. 1998. Sorption of dye from aqueous solution by peat. Chem. Eng. J. 70: 115–124.

Hoare, T.R. and D.S. Kohane. 2008. Hydrogels in drug delivery: Progress and challenges. Polymer 49: 1993–2007.

Hoffman, A.S. 2002. Hydrogels for biomedical applications. Adv. Drug Deliv. Rev. 43: 3–12.

Huang, D., W. Wang, Y. Kang, and A. Wang. 2012. Efficient adsorption and recovery of Pb(II) from aqueous solution by a granular pH-sensitive chitosan-based semi-IPN hydrogel. J. Macromol. Sci. Part A: Pure Appl. Chem. 49: 971–979.

Huang, X.Y., X.Y. Mao, H.T. Bu, X.Y. Yu, G.B. Jiang, and M.H. Zeng. 2011a. Chemical modification of chitosan by tetraethylenepentamine and adsorption study for anionic dye removal. Carbohydr. Res. 346: 1232–1240.

Huang, Y., M. Liu, L. Wang, C. Gao, and S. Xi. 2011b. A novel triple-responsive poly(3acrylamidephenylboronic acid-co-2-(dimethylamino) ethyl methacrylate)/(b-cyclodextrin-epichlorohydrin) hydrogels: Synthesis and controlled drug delivery. React. Funct. Polym. 71: 666–673.

Ilavsky, M., J. Hrouz, J. Stejskal, and K. Bouchal. 1984. Phase transition in swollen gels. 6. Effect of aging on the extent of hydrolysis of aqueous polyacrylamide solutions and on the collapse of gels. Macromolecules 17: 2868–2874.

Jain, E. and A. Kumar. 2009. Designing supermacroporous cryogels based on polyacrylonitrile and a polyacrylamide-chitosan semi-interpenetrating network. J. Biomater. Sci. 20: 877–902.

Jeon, Y.S., J. Lei, and J.-H. Kim. 2008. Dye adsorption characteristics of alginate/polyaspartate hydrogels. J. Ind. Eng. Chem. 14: 726–731.

Jin, S., F. Bian, M. Liu, S. Chen, and H. Liu. 2009. Swelling mechanism of porous P(VP-coMAA)/PNIPAM semi-IPN hydrogels with various pore sizes prepared by a freeze treatment. Polym. Int. 58: 142–148.

Jin, S., Y. Wang, J. He, Y. Yang, X. Yu, and G. Yue. 2013. Preparation and properties of a degradable interpenetrating polymer network based on starch with water retention, amelioration of soil, and slow release of nitrogen and phosphorus fertilizer. J. Appl. Polym. Sci. 128: 407–415.

Junyan, P., W. Sui, and Z. Ruifeng. 2006. Ion-imprinted IPNs for preconcentration and determination of Cd(II) by ame atomic absorption spectrometry. Chem. Anal. (Warsaw) 51: 701–713.

Keshavara Murthy, P.S., Y. Murali Mohan, J. Sreeramulu, and K. Mohana Raju. 2006. SemiIPNs of starch and poly(acrylamide-co-sodium methacrylate): Preparation, swelling and diffusion characteristics evaluation. React. Funct. Polym. 66: 1482–1493.

Kim, S.J., C.K. Lee, and S.I. Kim. 2004a. Characterization of the water state of hyaluronic acid and poly(vinyl alcohol) interpenetrating polymer networks. J. Appl. Polym. Sci. 92: 1467–1472.

Kim, S.J., S.R. Shin, Y.M. Lee, and S.I. Kim. 2003. Swelling characterizations of chitosan and polyacrylonitrile semi-interpenetrating polymer network hydrogels. J. Appl. Polym. Sci. 87: 2011–2015.

Kim, S.J., S.R. Shin, G.M. Spinks, I.Y. Kim, and S.I. Kim. 2005. Synthesis and characteristics of a semi-interpenetrating polymer network based on chitosan/polyaniline under different pH conditions. J. Appl. Polym. Sci. 96: 867–873.

Kim, S.J., S.G. Yoon, Y.H. Lee, and S.I. Kim. 2004b. Bending behavior of hydrogels composed of poly(methacrylic acid) and alginate by electrical stimulus. Polym. Int. 53: 1456–1460.

Krezovic, B.D., S.I. Dimitrijevic, J.M. Filipovic, R.R. Nikolic, and S.Lj. Tomic. 2013. Antimicrobial P(HEMA/IA)/PVP semi-interpenetrating network hydrogels. Polym. Bull. 70: 809–819.

Kuila, S.B. and S.K. Ray. 2012. Sorption and permeation studies of tetrahydrofuran-water mixtures using full interpenetrating network membranes. Sep. Purif. Technol. 89: 39–50.

Kumar, K.V. and S. Sivanesan. 2006. Equilibrium data, isotherm parameters and process design for partial and complete isotherm of methylene blue onto activated carbon. J. Hazard. Mater. B134: 237–244.

Kundakci, S., E. Karadag, and O.B. Üzüm. 2011. Investigation of swelling/sorption characteristics of highly swollen AAm/AMPS hydrogels and semi IPNs with PEG as biopotential sorbent. J. Encapsul. Adsorpt. Sci. 1: 7–22.

Kusuktham, B. 2006. Preparation of interpenetrating polymer network gel beads for dye adsorption. J. Appl. Polym. Sci. 102: 1585–1591.

Lagergren, S. 1898. Kungliga svenska vetenskapsakademiens. Handlingar 24: 1–39.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40: 1361–1403.

Lee, S.B., E.K. Park, Y.M. Lim, S.K. Cho, S.Y. Kim, Y.M. Lee, and Y.C. Nho. 2006. Preparation of alginate/poly(n-isopropylacrylamide) semi-interpenetrating and fully interpenetrating polymer network hydrogels with γ-ray irradiation and their swelling behaviors. J. Appl. Polym. Sci. 100: 4439–4446.

Lee, Y., D.N. Kim, D. Choi, W. Lee, J. Park, and W.-G. Koh. 2008. Preparation of interpenetrating polymer network composed of poly(ethylene glycol) and poly(acrylamide) hydrogels as a support of enzyme immobilization. Polym. Adv. Technol. 18: 852–858.

Li, S. 2010. Removal of crystal violet from aqueous solution by sorption into semiinterpenetrated networks hydrogels constituted of poly(acrylic acid-acryamidemethacrylate) and amylose. Bioresour. Technol. 101: 2197–2202.

Li, X., W. Wu, and W. Liu. 2008a. Synthesis and properties of thermo-responsive guar gum/ poly(N-isopropylacrylamide) interpenetrating polymer network hydrogels. Carbohydr. Polym. 71: 394–402.

Li, X., S. Xu, Y. Pen, and J. Wang. 2008b. The swelling behaviors and network parameters of cationic starch-g-acrylic acid/poly(dimethyldiallylammonium chloride) semiinterpenetrating networks hydrogels. J. Appl. Polym. Sci. 110: 1828–1836.

Li, X., S. Xu, J. Wang, X. Chen, and S. Feng. 2009. Structure and characterization of amphoteric semi-IPN hydrogel based on cationic starch. Carbohydr. Polym. 75: 688–693.

Liang, S., L. Liu, Q. Huang, and K.L. Yam. 2009. Preparation of single or double-network chitosan/poly(vinyl alcohol) gel films through selectively cross-linking method. Carbohydr. Polym. 77: 718–724.

Limousin, G., J.-P. Gaudet, L. Charlet, S. Szenknect, V. Barthes, and M. Krimissa. 2007. Sorption isotherms: A review on physical bases, modeling and measurement. Appl. Geochem. 22: 249–275.

Lin, H., J. Zhou, C. Yingde, and S. Gunasekaran. 2010. Synthesis and characterization of ph- and salt-responsive hydrogels based on etherificated sodium alginate. J. Appl. Polym. Sci. 115: 3161–3167.

Liu, J., W. Wang, and A. Wang. 2011. Synthesis, characterization, and swelling behaviors of chitosan-g-poly(acrylic acid)/poly(vinyl alcohol) semi-IPN superabsorbent hydrogels. Polym. Adv. Technol. 22: 627–634.

Liu, M., H. Su, and T. Tan. 2012a. Synthesis and properties of thermo- and pH-sensitive poly(N-isopropylacrylamide)/polyaspartic acid IPN hydrogels. Carbohydr. Polym. 87: 2425–2431.

Liu, X., H. Guo, and L. Zha. 2012b. Study of pH/temperature dual stimuli-responsive nanogels with interpenetrating polymer network structure. Polym. Int. 61: 1144–1159.

Liu, Y., X. Cao, R. Hua, Y. Wang, Y. Liu, C. Pang, and Y. Wang. 2010. Selective adsorption of uranyl ion on ion-imprinted chitosan/PVA cross-linked hydrogel. Hydrometallurgy 104: 150–155.

Lozinsky, V.I., I.Y. Galaev, F.M. Plieva, I.N. Savina, H. Jungvid, and B. Mattiasson. 2003. Polymeric cryogels as promising materials of biotechnological interest. Trends Biotechnol. 21: 445–451.

Mahdavinia, G.R., G.B. Marandi, A. Pourjavadi, and G. Kiani. 2010. Semi-IPN carrageenanbased nanocomposite hydrogels: Synthesis and swelling behavior. J. Appl. Polym. Sci. 118: 2989–2997.

Mahou, R. and C. Wandrey. 2010. Alginate-poly(ethylene glycol) hybrid microspheres with adjustable physical properties. Macromolecules 43: 1371–1378.

Mallikarjuna Reddy, K., V. Ramesh Babu, K.S.V. Krishna Rao, M.C.S. Subha, K. Chowdoji Rao, M. Sairam, and T.M. Aminabhavi. 2008. Temperature sensitive semi-IPN microspheres from sodium alginate and n-isopropylacrylamide for controlled release of 5-fluorouracil. J. Appl. Polym. Sci. 107: 2820–2829.

Mandal, B. and S.K. Ray. 2013. Synthesis of interpenetrating network hydrogel from poly(acrylic acid-co-hydroxyethyl methacrylate) and sodium alginate: Modeling and kinetics study for removal of synthetic dyes from water. Carbohydr. Polym. 98: 257–269.

Mandal, B., S.K. Ray, and R. Bhattacharyya. 2012. Synthesis of full and semi interpenetrating hydrogel from polyvinyl alcohol and poly (acrylic acid-co-hydroxyethylmethacrylate) copolymer: Study of swelling behavior, network parameters, and dye uptake properties. J. Appl. Polym. Sci. 124: 2250–2268.

Marsano, E., E. Bianchi, S. Vicini, L. Compagnino, A. Sionkowska, J. Skopinska, and M. Wisniewski. 2005. Stimuli responsive gels based on interpenetrating network of chitosan and poly(vinylpyrrolidone). Polymer 46: 1595–1600.

Martinez, L., F. Agnely, R. Bettini, M. Besnard, P. Colombo, and G. Couarraze. 2004. Preparation and characterization of chitosan based micro networks: Transposition to a prilling process. J. Appl. Polym. Sci.

93: 2550–2558.

M'Bareck, C.O., Q.T. Nguyen, S. Alexandre, and I. Zimmerlin. 2006. Fabrication of ionexchange ultrafiltration membranes for water treatment I. Semi-interpenetrating polymer networks of polysulfone and poly(acrylic acid). J. Membr. Sci. 278: 10–18.

Milosavljevic, N.B., N.Z. Milasinovic, I.G. Popovic, J.M. Filipovic, and M.T.K. Krusic. 2011. Preparation and characterization of pH-sensitive hydrogels based on chitosan, itaconic acid and methacrylic acid. Polym. Int. 60: 443–452.

Myung, D., D. Waters, M. Wiseman, P.-E. Duhamel, J. Noolandi, C.N. Ta, and C.W. Frank. 2008. Progress in the development of interpenetrating polymer network hydrogels. Polym. Adv. Technol. 19: 647–657.

Park, H.C., R.M. Meertens, M.H.V. Mulder, and C.A. Smolders. 1994. Pervaporation of alcohol–toluene mixtures through polymer blend membranes of poly(acrylic acid) and poly(vinyl alcohol). J. Membr. Sci. 90: 265–274.

Peak, C.W., J.J. Wilker, and G. Schmidt. 2013. A review on tough and sticky hydrogels. Colloid Polym. Sci. 291: 2031–2047.

Peppas, N.A., P. Bures, W. Leobandung, and H. Ichikawa. 2000. Hydrogels in pharmaceutical formulations. Eur. J. Pharm. Biopharm. 50: 27–46.

Perju, M.M., M.V. Dinu, and E.S. Drăgan. 2012. Sorption of Methylene Blue onto ionic composite hydrogels based on polyacrylamide and dextran sulfate: Kinetics, isotherms and thermodynamics. Sep. Sci. Technol. 47: 1322–1333.

Pescosolido, L., T. Vermonden, J. Malda, R. Censi, W.J.A. Dhert, F. Alhaique, W.E. Hennink, and P. Matricardi. 2011. In situ forming IPN hydrogels of calcium alginate and dextranHEMA for biomedical applications. Acta Biomater. 7: 1627–1633.

Plieva, F.M., M. Karlsson, M.R. Aguilar, D. Gomez, S. Mikhalovsky, and I.Y. Galaev. 2005. Pore structure in supermacroporous polyacrylamide based cryogels. Soft Matter 1: 303–309.

Ramesh Babu, V., C. Kim, S. Kim, C. Ahn, and Y.-I. Lee. 2010. Development of semiinterpenetrating carbohydrate polymeric hydrogels embedded silver nanoparticles and its facile studies on E. coli. Carbohydr. Polym. 81: 196–202.

Reis, A.V., M.R. Guilherme, T.A. Moia, L.H.C. Mattoso, E.C. Muniz, and E.B. Tambourgi. 2008. Synthesis and characterization of a starch-modi�ed hydrogel as potential carrier for drug delivery system. J. Polym. Sci. Part A: Polym. Chem. 46: 2567–2574.

Rodriguez, D.E., J. Romero-Garcia, E. Ramirez-Vargas, A.S. Ledezma-Perez, and E. AriasMarin. 2006. Synthesis and swelling characteristics of semi-interpenetrating polymer network hydrogels composed of poly(acrylamide) and poly(γ-glutamic acid). Mater. Lett. 60: 1390–1393.

Samanta, H.S. and S.K. Ray. 2014. Synthesis, characterization, swelling and drug release behavior of semi-interpenetrating network hydrogels of sodium alginate and polyacrylamide. Carbohydr. Polym. 67: 666–678.

Shi, J., N.M. Alves, and J.F. Mano. 2006. Drug release of pH/temperature-responsive calcium alginate/poly(N-isopropylacrylamide) semi-IPN beads. Macromol. Biosci. 6: 358–363.

Silan, C., A. Akcali, M.T. Otkun, N. Ozbey, S. Butun, O. Ozay, and N. Sahiner. 2012. Novel hydrogel particles and their IPN �lms as drug delivery systems with antibacterial properties. Colloids Surf. B: Biointerfaces 89: 245–253.

Singha, N.R., S. Kar, S. Ray, and S.K. Ray. 2009a. Separation of isopropyl alcohol-water mixtures by pervaporation using crosslink IPN membranes. Chem. Eng. Process.: Process Intensification 48: 1020–1029.

Singha, N.R., S.B. Kuila, P. Das, and S.K. Ray. 2009b. Separation of toluene-methanol mixtures by pervaporation using crosslink IPN membranes. Chem. Eng. Process.: Process Intensification 48: 1560–1565.

Solak, E.K. 2011. Preparation and characterization of IPN microspheres for controlled delivery of naproxen. J. Biomater. Nanobiotechnol. 2: 445–453.

Şolpan, D. and M. Torun. 2005. Investigation of complex formation between (sodium alginate/ acrylamide) semi-interpenetrating polymer networks and lead, cadmium, nickel ions. Colloids Surf. A 268: 12–18.

Şolpan, D., M. Torun, and O. Güven. 2008. The usability of (sodium alginate/acrylamide) semi-interpenetrating polymer networks on removal of some textile dyes. J. Appl. Polym. Sci. 108: 3787-3795.

Sperling, L.H. 1994. Interpenetrating polymer networks: An overview. In Interpenetrating Polymer Networks, D. Klempner, L.H. Sperling, and L.A. Utracki (eds.). American Chemical Society, Washington, DC, pp. 3–38.

Sperling, L.H. 2005. Interpenetrating polymer networks. In Encyclopedia of Polymer Science and Technology, H.F. Mark (ed.). John Wiley & Sons, New York, Vol. 10, pp. 272–311.

Srivastava, Y.C., M.M. Swamy, I.D. Mall, B. Prasad, and I.M. Mishra. 2006. Adsorptive removal of phenol by bagasse y ash and activated carbon: Equilibrium, kinetics and thermodynamics. Colloids Surf. A 272: 89–104.

Tang, Q., J. Wu, and J. Lin. 2008. A multifunctional hydrogel with high conductivity, pH-responsive, thermo-responsive and release properties. Carbohydr. Polym. 73: 315–321.

Thimma Reddy, T. and A. Takahara. 2009. Simultaneous and sequential micro-porous semiinterpenetrating polymer network hydrogel �lms for drug delivery and wound dressing applications. Polymer 50: 3537–3546.

Üzüm, U.B. and E. Karadağ. 2012. Equilibrium swelling studies and dye sorption characterization of AAm/SA hydrogels cross-linked by PEGDMA and semi-IPNs with PEG. Adv. Polym. Technol. 31: 141–153.

Üzüm, U.B. and E. Karadağ. 2013. Water and dye sorption studies of novel semi-IPNs: Acrylamide/4styrenesulfonic acid sodium salt/PEG hydrogels. Polym. Eng. Sci. 53: 1262–1271.

Wan Ngah, W.S., L.C. Teong, and M.A.K.M. Hana�ah. 2011. Adsorption of dyes and heavy metals by chitosan composites: A review. Carbohydr. Polym. 83: 1446–1456.

Wang, B., M.-Z. Liu, R. Liang, S.-L. Ding, Z.-B. Chen, S.-L. Chen, and S.-P. Jin. 2008. MMTCA recognition by molecular imprinting in interpenetrating polymer network hydrogels based on poly(acrylic acid) and poly(vinyl alcohol). Macromol. Biosci. 8: 417-425.

Wang, J., F. Liu, and J. Wei. 2011a. Enhanced adsorption properties of interpenetrating polymer network hydrogels for heavy metal ion removal. Polym. Bull. 67: 1709–1720.

Wang, J., X. Zhou, and H. Xiao. 2013a. Structure and properties of cellulose/poly(Nisopropylacrylamide) hydrogels prepared by SIPN strategy. Carbohydr. Polym. 94: 749–754.

Wang, J.J. and F. Liu. 2012. UV-curing of simultaneous interpenetrating network silicone hydrogels with hydrophilic surface. Polym. Bull. 69: 685–697.

Wang, J.J. and F. Liu. 2013. Enhanced adsorption of heavy metal ions onto simultaneous interpenetrating polymer network hydrogels synthesized by UV irradiation. Polym. Bull. 70: 1415–1430.

Wang, Q., J. Zhang, and A. Wang. 2009. Preparation and characterization of a novel pHsensitive chitosan-g-poly(acrylic acid)attapulgite/sodium alginate composite hydrogel bead for controlled release of diclofenac sodium. Carbohydr. Polym. 78: 731–737.

Wang, W., D. Huang, Y. Kang, and A. Wang. 2013b. One-step in situ fabrication of granular semi-IPN hydrogel based on chitosan and gelatin for fast and efficient adsorption of Cu 2+ ion. Colloids Surf. B: Biointerfaces 106: 51–59.

Wang, W., Y. Kang, and A. Wang. 2013c. One-step fabrication in aqueous solution of a granular alginate-based hydrogel for fast and efficient removal of heavy metal ions. J. Polym. Res. 20: 110.

Wang, W. and A. Wang. 2010. Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly(sodium acrylate) and polyvinylpyrrolidone. Carbohydr. Polym. 80: 1028–1036.

Wang, W., Q. Wang, and A. Wang. 2011b. pH-responsive carboxymethylcellulose-g-poly(sodium acrylate)/poly(vinylpyrrolydone) semi-IPN hydrogels with enhanced responsive and swelling properties. Macromol. Res. 19: 57–65.

Wawrzkiewicz, M. 2013. Removal of C.I. Basic Blue 3 dye by sorption onto cation exchange resin, functionalized and non-functionalized polymeric sorbents from aqueous solutions and wastewaters. Chem. Eng. J. 217: 414–425.

Weber Jr., W.J. and J.C. Morris. 1963. Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div.

Am. Soc. Chem. Eng. 89: 31–59.

Wei, J., S. Xu, R. Wu, J. Wang, and Y. Gao. 2007. Synthesis and characterization of an amphoteric semi-IPN hydrogel composed of acrylic acid and poly(diallyldimethylammonium chloride). J. Appl. Polym. Sci. 103: 345–350.

Xiao, C., H. Li, and Y. Gao. 2009. Preparation of fast pH-responsive ferric carboxymethylcellulose/poly(vinyl alcohol) double-network microparticles. Polym. Int. 58: 112–115.

Yamashita, K., T. Nishimura, and M. Nango. 2003. Preparation of IPN-type stimuli-responsive heavy-metal-ion adsorbent gel. Polym. Adv. Technol. 14: 189–194.

Yang, J., J. Chen, D. Pan, Y. Wan, and Z. Wang. 2013. pH-sensitive interpenetrating network hydrogels based on chitosan derivatives and alginate for oral drug delivery. Carbohydr. Polym. 92: 719–725.

Yin, L., L. Fei, F. Cui, C. Tang, and C. Yin. 2007a. Superporous hydrogels containing poly(acrylic-co-acrylamide)/O-carboxymethyl chitosan interpenetrating polymer networks. Biomaterials 28: 1258–1266.

Yin, L., L. Fei, F. Cui, C. Tang, and C. Yin. 2007b. Synthesis, characterization, mechanical properties and biocompatibility of interpenetrating polymer network-superporous hydrogel containing sodium alginate. Polym. Int. 56: 1563–1571.

Yin, L., Z. Zhao, Y. Hu, J. Ding, F. Cui, C. Tang, and C. Yin. 2008. Polymer-protein interaction, water retention, and biocompatibility of a stimuli-sensitive superporous hydrogel containing interpenetrating polymer network. J. Appl. Polym. Sci. 108: 1238–1248.

Zadrazil, A. and F. Stepanek. 2010. Investigation of thermo-responsive optical properties of a composite hydrogel. Colloids Surf. A 372: 115–119.

Zhang, G.Q., L.S. Zha, M.H. Zhou, J.H. Ma, and B.R. Liang. 2005. Preparation and characterization of pH- and temperature responsive semi-interpenetrating polymer network hydrogels based on linear sodium alginate and crosslinked poly(N-isopropylacrylamide). J. Appl. Polym. Sci. 97: 1931–1940.

Zhang, J.-T., R. Bhat, and K.D. Jandt. 2009. Temperature-sensitive PVA/PNIPAAm semi-IPN hydrogels with enhanced responsive properties. Acta Biomater. 5: 488–497.

Zhang, N., M. Liu, Y. Shen, J. Chen, L. Dai, and C. Gao. 2011. Preparation, properties, and drug release of thermo- and pH-sensitive poly(2-dimethylamino)ethyl methacrylate)/poly(N,N-diethylacrylamide) semi-IPN hydrogels. J. Mater. Sci. 46: 1523–1534.

Zhao, G., X. Wu, X. Tan, and X. Wang. 2011. Sorption of heavy metal ions from aqueous solutions: A review. Open Colloid Interface J. 4: 19–31.

Zhao, Q., J. Sun, Y. Lin, and Q. Zhou. 2010. Study of the properties of hydrolyzed polyacrylamide hydrogels with various pore structures and rapid pH-sensitivities. React. Funct. Polym. 70: 602–609.

Zhao, S., F. Zhou, L. Li, M. Cao, D. Zuo, and H. Liu. 2012. Removal of anionic dyes from aqueous solutions by adsorption of chitosan-based semi-IPN hydrogel composites. Composites Part B: Eng. 43: 1570–1578.

Zhao, Y., J. Kang, and T. Tan. 2006. Salt-, pH-, and temperature-responsive semi-interpenetrating polymer network hydrogel based on poly(aspartic acid) and poly(acrylic acid). Polymer 47: 7702–7710.

Zhou, C. and Q. Wu. 2011. A novel polyacrylamide nanocomposite hydrogel reinforced with natural chitosan nano�bers. Colloids Surf. B: Biointerfaces 84: 155–162.

12 Chapter 12: Toward Adaptive Self-Informed Membranes

Agre, P. 2004. Aquaporin water channels. Angew. Chem. Int. Ed. 43: 4278–4290.

Arnal-Hérault, C., M. Barboiu, A. Pasc, M. Michau, P. Perriat, and A. van der Lee. 2007c. Constitutional self-organization of adenine-uracil-derived hybrid materials. Chem. Eur. J. 1: 6792–6800.

Arnal-Herault, C., M. Barboiu, E. Petit, M. Michau, and A. van der Lee. 2005. Cation-π interaction: A case for macrocycle-cation π-interaction by its ureidoarene counteranion. New J. Chem. 29: 1535–1539.

Arnal-Herault, C., A. Pasc-Banu, M. Barboiu, M. Michau, and A. van der Lee. 2007a. Amplification and transcription of the dynamic supramolecular chirality of the G-quadruplex. Angew. Chem. Int. Ed. 46: 4268–4272.

Arnal-Herault, C., A. Pasc-Banu, M. Michau, D. Cot, E. Petit, and M. Barboiu. 2007b. Functional G-quartet macroscopic membrane films. Angew. Chem. Int. Ed. 46: 8409–8413.

Barboiu, M. 2004. Supramolecular polymeric macrocyclic receptors—Hybrid carrier vs. channel transporters in bulk liquid membranes. J. Inclusion Phenom. Macrocyclic Chem. 49: 133–137.

Barboiu, M. 2010. Dynamic interactive systems—Dynamic selection in hybrid organicinorganic constitutional networks. Chem. Commun. 46: 7466–7476.

Barboiu, M. (ed.). 2012. Constitutional dynamic chemistry. In Topics in Current Chemistry. Berlin/Heidelberg: Springer-Verlag.

Barboiu, M., S. Cerneaux, G. Vaughan, and A. van der Lee. 2004. Ion-driven ATP-pump by self-organized hybrid membrane materials. J. Am. Chem. Soc. 126: 3545–3550.

Barboiu, M., C. Guizard, N. Hovnanian, J. Palmeri, C. Reibel, C. Luca, and L. Cot. 2000a. Facilitated transport of organics of biological interest I. A new alternative for the amino acids separations by fixed-site crown-ether polysiloxane membranes. J. Membr. Sci., 172: 91–103.

Barboiu, M., C. Guizard, C. Luca, A. Albu, N. Hovnanian, and J. Palmeri. 1999. A new alternative to amino acid transport: Facilitated transport of l-phenylalanine by hybrid siloxane membrane containing a fixed site macrocyclic complexant. J. Membr. Sci. 161: 193–206.

Barboiu, M., C. Guizard, C. Luca, N. Hovnanian, J. Palmeri, and L. Cot. 2000. Facilitated transport of organics of biological interest II. Selective transport of organic acids by macrocyclic fixed site complexant membranes. J. Membr. Sci. 174: 277–286.

Barboiu, M. and J.-M. Lehn. 2002. Dynamic chemical devices. Modulation of contraction/ extension molecular motion by coupled ion binding/pH change induced structural switching. Proc. Natl. Acad. Sci. USA 99: 5201–5206.

Barboiu, M., C. Luca, C. Guizard, N. Hovnanaian, L. Cot, and G. Popescu. 1997. Hybrid organic-inorganic fixed site dibenzo-18-crown complexant membranes. J. Membr. Sci. 129: 197–207.

Barboiu, M., G. Vaughan, and A. van der Lee. 2003. Self-organised heteroditopic macrocyclic superstructures. Org. Lett. 5: 3073–3076.

Calzolari, A., R. Di Felice, and E. Molinari. 2004. Electronic properties of guanine-based nanowires. Solid State Commun. 131: 557–567.

Cazacu, A., M. Barboiu, M. Michau, R. Caraballo, C. Arnal-Herault, and A. Pasc-Banu. 2008. Functional organic–inorganic hybrid membranes. Chem. Eng. Process. 47: 1044–1052.

Cazacu, A., Y.M. Legrand, A. Pasc, G. Nasr, A. van der Lee, E. Mahon, and M. Barboiu. 2009. Dynamic hybrid materials for constitutional selective membranes. Proc. Natl. Acad. Sci. USA 106: 8117–8122.

Cazacu, A., C. Tong, A. van der Lee, T.M. Fyles, and M. Barboiu. 2006. Columnar selfassembled ureidocrown-ethers—An example of ion-channel organization in lipid bilayers. J. Am. Chem. Soc. 128: 9541–9548.

Cohen, H., T. Sapir, N. Borovok, T. Molotosky, R. Di Felice, A.B. Kotylar, and D. Porath. 2007. Polarizability of G4-DNA observed by electrostatic force microscopy measurements. Nano Lett. 7: 981–986.

Gallivan, J.P. and D.A. Dougherty. 1999. Cation-π interactions in structural biology. Proc. Natl. Acad. Sci. USA 96: 9459–9464.

Gokel, G.W. and E. Abel. 1996. Complexation of organic cations. In Comprehensive Supramolecular Chemistry, Vol. 1, J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vögtle, and K.S. Suslick (eds.). Oxford, U.K.: Pergamon, pp. 511–534.

MacKinnon, R. 2004. Potassium channels and the atomic basis of selective ion conduction (Nobel Lecture). Angew. Chem. Int. Ed. 43: 4265–4289.

Michau, M. and M. Barboiu. 2009. Self-organized proton conductive layers in hybrid proton exchange membranes, exhibiting high ionic conductivity. J. Mater. Chem. 19: 6124–6131.

Michau, M., M. Barboiu, R. Caraballo, C. Arnal-Hérault, and A. van der Lee. 2008. Directional ion-conduction pathways in self-organized hybrid membranes. Chem. Eur. J. 14: 1776–1783.

Mihai, S., Y. Le Duc, D. Cot, and M. Barboiu. 2010. Sol-gel selection of hybrid G-quadruplex architectures from dynamic supramolecular guanosine libraries. J. Mater. Chem. 20: 9443–9448.

Sanchez, C., B. Julian, P. Belleville, and M. Popall. 2005. Applications of hybrid organicinorganic nanocomposites. J. Mater. Chem. 15: 3559–3592.

van Bommel, K.J.C., A. Frigerri, and S. Shinkai. 2003. Organic templates for the generation of inorganic materials. Angew. Chem. Int. Ed. 42: 980–999.